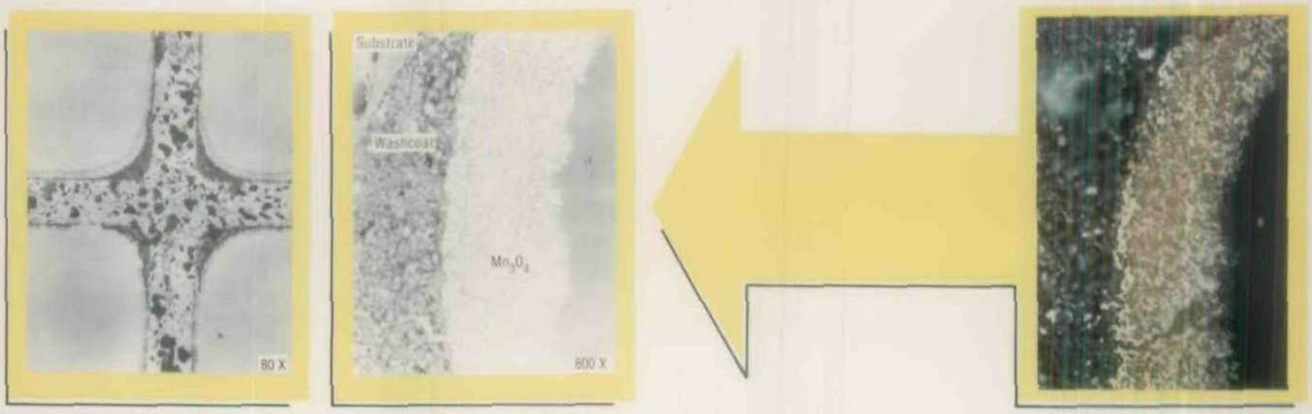
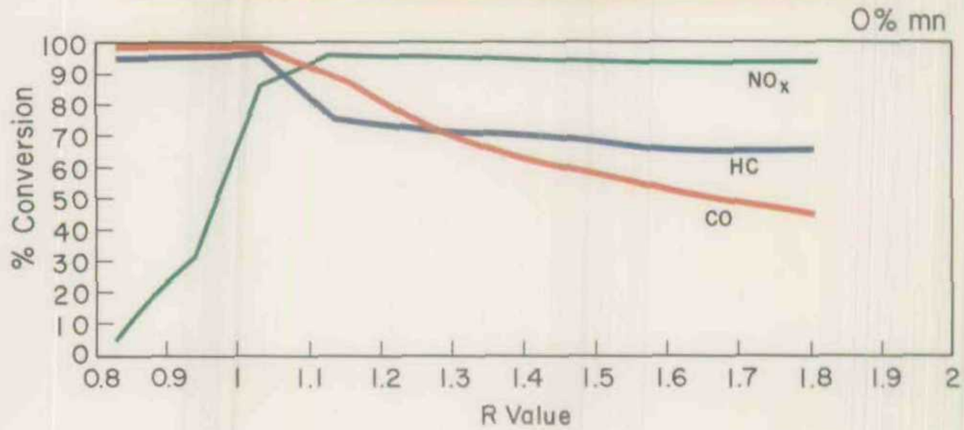
A-90-16
IV-D-59

Effect Of MMT On Catalyst

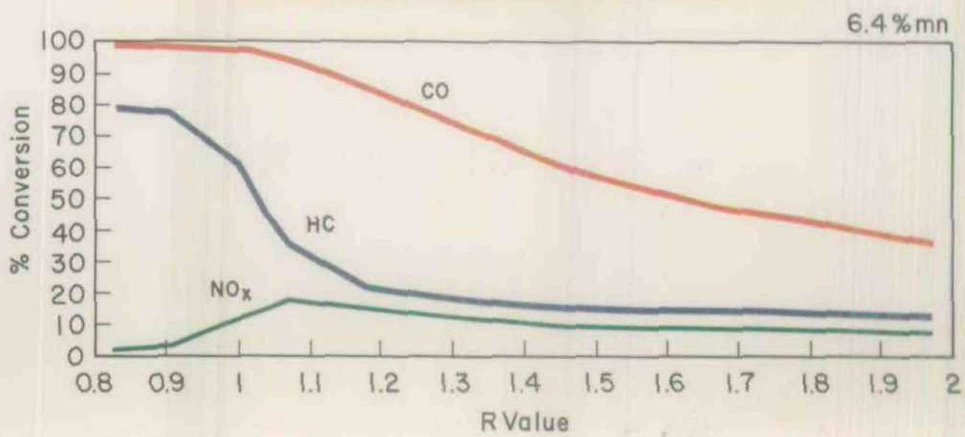


Optical Micrograph of Catalyst (33,000 miles)

Catalyst Activity - Non MMT Fueled
3.0 L 86 Taurus 46,000 Miles



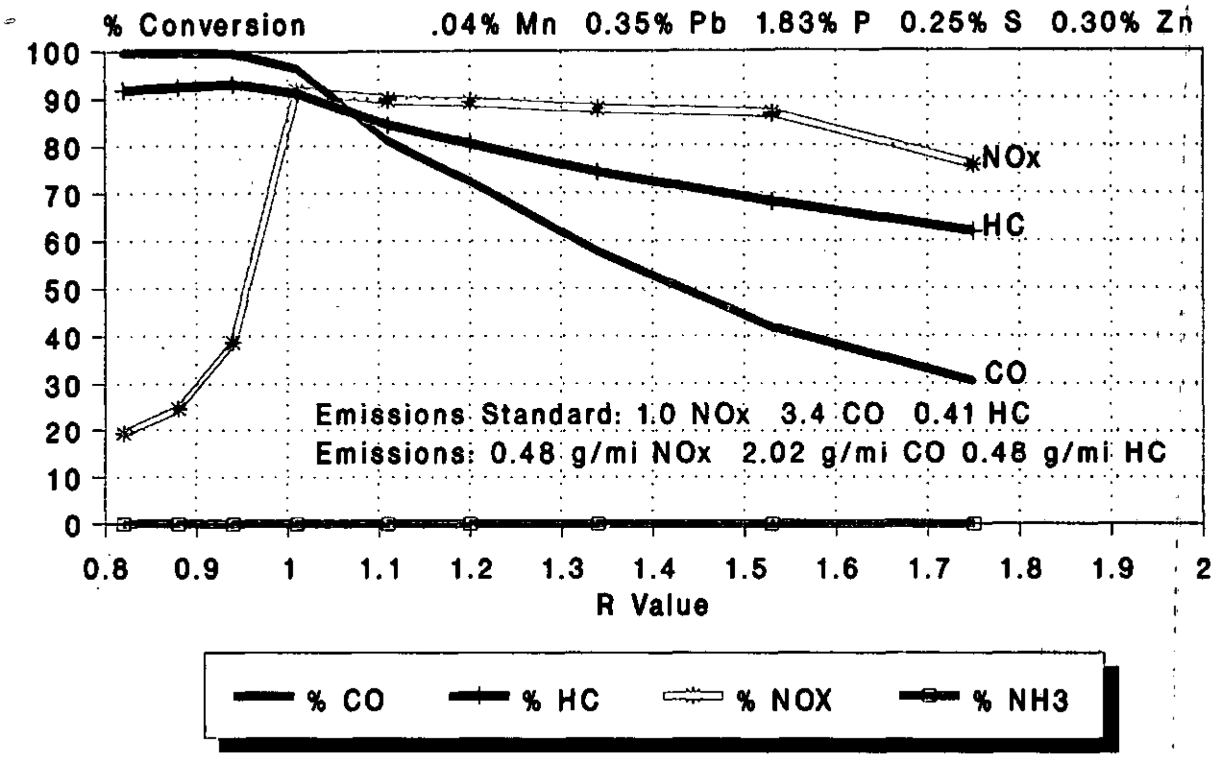
Catalyst Activity - MMT Fueled
2.3 L Ranger - 33,000 Miles



A-90-16
IV-D-59

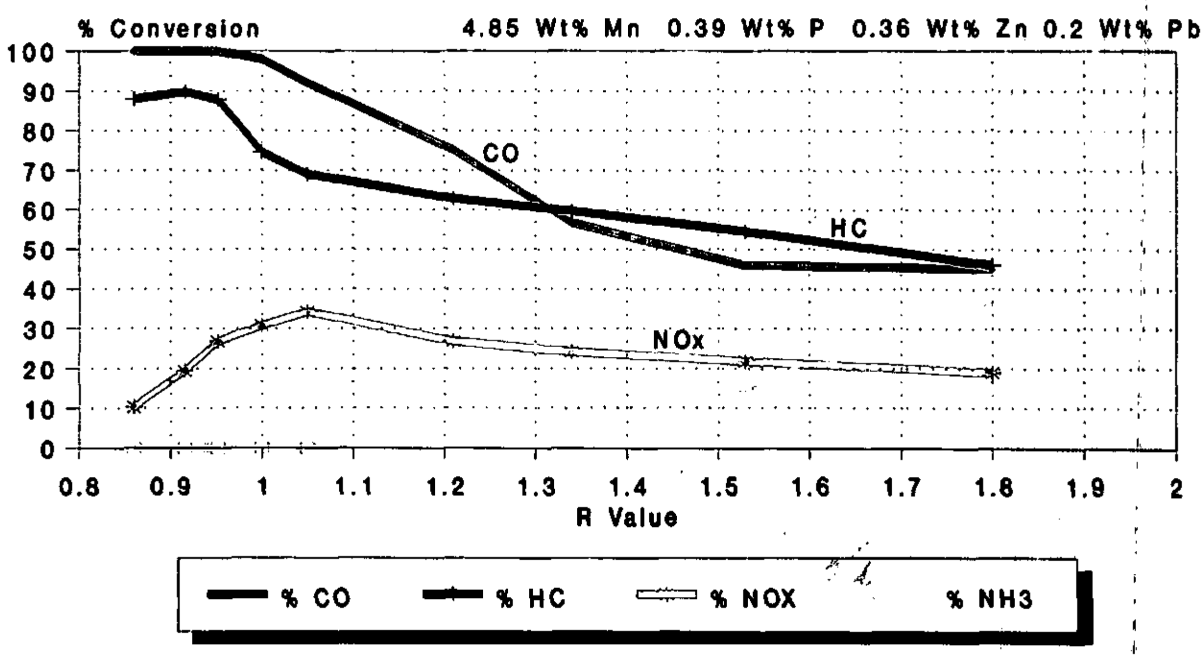
Catalyst Activity - Non MMT Fueled

1.6L 83 Escort 38,792 miles



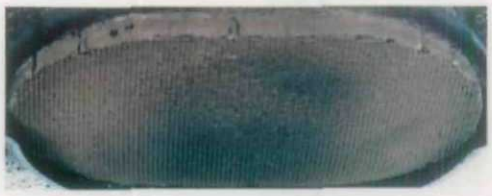
Catalyst Activity - MMT Fueled

1.9L 86 Escort EFI 32,319 miles (104)



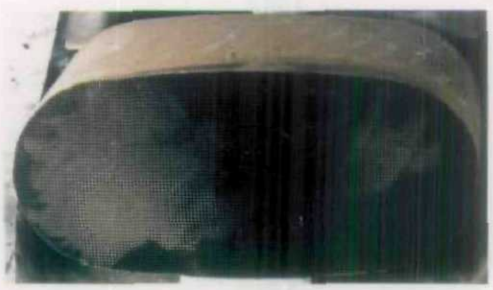
A-90-16
IV-D-59

Effects Of MMT On Catalysts



1986 2.3L Topaz
23,744 Miles
1.4% Mn

1984 2.3L Ranger
32,879 Miles
6.1% Mn



1984 2.3L Ranger
32,879 Miles
6.1% Mn

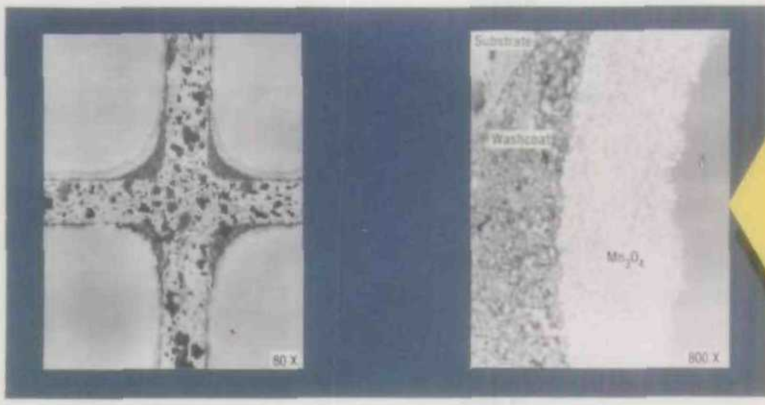
1985 2.3L Merkur
32,088 Miles
1.7% Mn

1987 5.8L LTD
(Police)
58,000 Miles
5.1 % Mn

A-90-16
IV-D-59

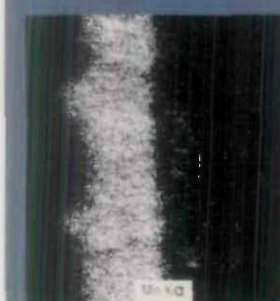
Effect Of MMT On Catalyst

Optical and SEM



Optical
Micrograph
Of Catalyst
(33,000 miles)

SEM
Micrographs —
Cross-section
Of Catalyst
(1 cm = 10 microns)



Mn
Elemental Map —
Cross-section
Of Catalyst
(1 cm = 10 microns)

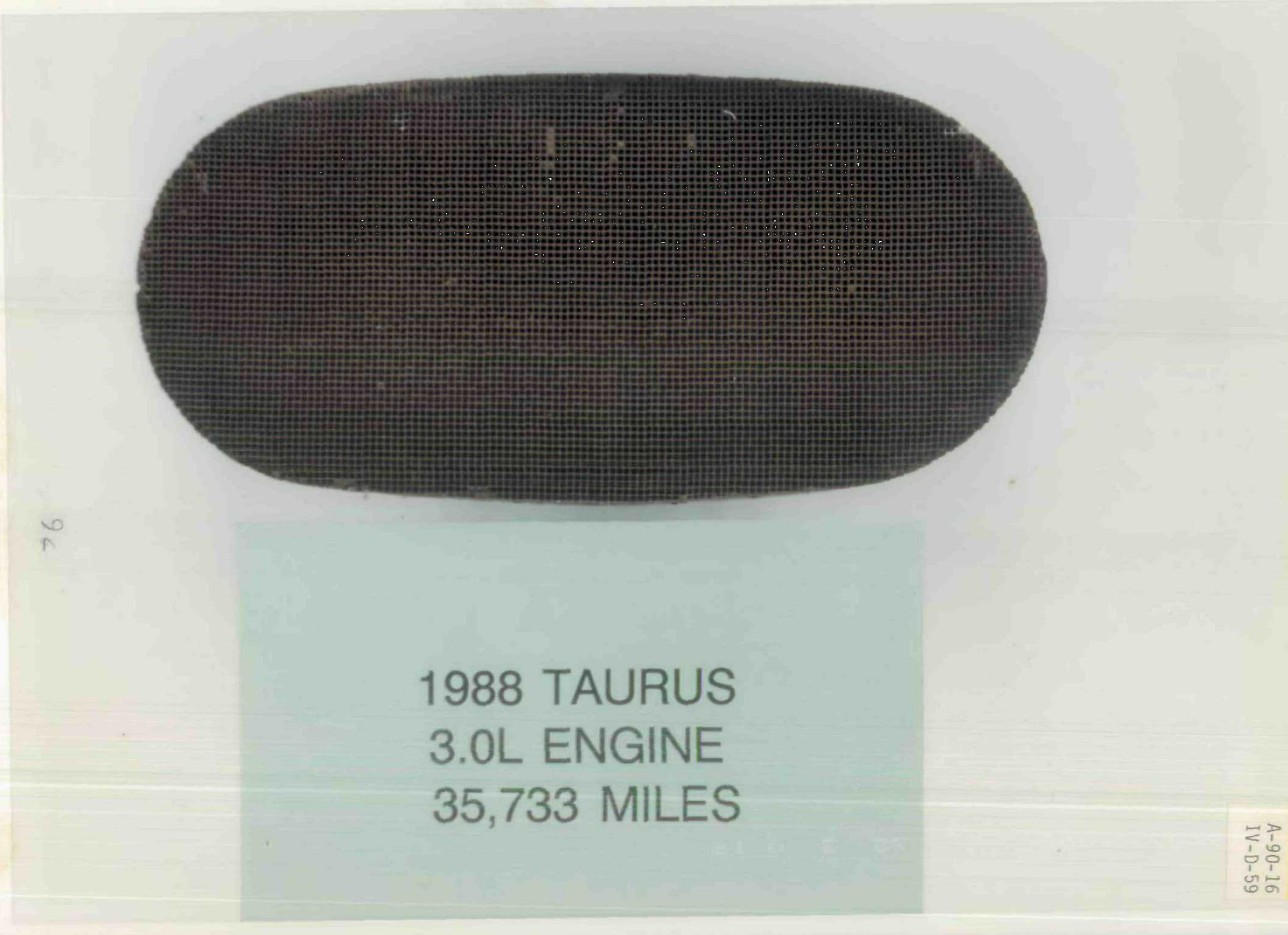
SEM
Micrographs —
Cross-section
Of Catalyst
(1 cm = 10 microns)

Mn
Elemental Map —
Cross-section
Of Catalyst
(1 cm = 10 microns)

SEM
Photomicrograph
Of Surface Morphology
At 33,000 In-use Miles
(1000 X)

A-90-16
IV-D-59

A-90-16
IV-D-59



96

A-90-16
IV-D-58

A-90-16
IV-D-59

95

1988 SABLE
3.8L ENGINE
62,224 MILE

A-90-16
IV-D-59

A-90-16
IV-D-59

A-90-16
IV-D-59

1988 TAURUS
3.0L ENGINE
39,662 MILE

A-90-16
IV-D-59

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ATTACHMENT 4

"RESULTS OF COORDINATING RESEARCH COUNCIL
MMT FIELD TEST PROGRAM" (SAE 790706)

SAE Technical Paper Series

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Results of Coordinating Research Council MMT Field Test Program

J. D. Benson
Fuels and Lubricants Department
General Motors Research Laboratories

R. J. Campion
Exxon Company U.S.A.

L. J. Painter
Chevron Research Company

JUL 23 1980
EPA AIR DOCKET

Passenger Car Meeting
Hyatt Regency, Dearborn
June 11-15, 1979

SOCIETY OF AUTOMOTIVE ENGINEERS, INC.
400 COMMONWEALTH DRIVE
WARRENDALE, PENNSYLVANIA 15096

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Results of Coordinating Research Council MMT Field Test Program

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SINCE 1975, MOST CARS PRODUCED IN THE U.S. have been equipped with catalytic converters for reducing exhaust emissions. These cars require the exclusive use of unleaded gasoline. As older cars are replaced by new, converter-equipped cars, the demand for unleaded gasoline increases. To meet this demand and provide the desired octane quality, petroleum refiners in 1976 began using the fuel antiknock additive methylcyclopentadienyl manganese tricarbonyl (MMT) in unleaded gasoline. A prior study (1)* and a review by the Environmental Protection Agency (2), had indicated that the use of MMT in unleaded gasoline did not adversely affect emissions, emission control systems, or other automotive components. The tests leading to these conclusions were carried out on vehicles equipped with first-generation oxidation catalysts; those vehicles were designed to meet the 1.5 g/mile hydrocarbon emission standard. As the use of MMT became more widespread, the EPA decided in 1977 (3) to include MMT in vehicle certification fuel for model year 1979. Concurrently, additional tests run by the automotive industry (4-5) had indicated that MMT increased hydrocarbon emissions and could, under some conditions, cause plugging of catalytic converters in advanced emission control systems. Thus, the automotive industry became concerned that they could not meet the 0.41 g/mile hydrocarbon standard as legislated for California in 1977 and nationwide by 1980.

The available data on MMT effects were reviewed extensively in early 1977, primarily at EPA-sponsored public meetings. These data from the automotive and petroleum industries and government laboratories were conflicting. To resolve this issue, the Coordinating Research Council (CRC), in mid-1977, undertook a comprehensive experimental program to determine whether MMT is detrimental to emission control in 1977-78 California vehicles. This cooperative CRC program was directed by technical representatives of the automotive and petroleum

*Numbers in parentheses designate References at end of paper.

ABSTRACT

The effect of the gasoline antiknock additive, MMT, on automotive emission control systems was studied in a 63-car field test. The cars were operated for 50 000 miles, and the effects of MMT on hydrocarbon, CO and NO_x emissions, catalyst plugging and spark plug life were determined.

Two concentration levels of MMT in a clear base fuel were studied, 1/32 g Mn/gal and 1/16 g Mn/gal. Seven 1977-78 model year cars, all calibrated to meet California standards, were included in the statistical design.

The results of this study indicate that the use of MMT at either test concentration increases both engine and tailpipe hydrocarbon emissions, compared to clear fuel. At 50K miles, the average tailpipe hydrocarbon increase was 0.09 g/mile for 1/32 MMT fuel, and 0.11 g/mile for 1/16 MMT fuel. This increase was pronounced at low mileage intervals, and significant differences continued for the duration of the test. CO and NO_x emissions, catalyst plugging, and spark plug life were not affected by MMT.

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industries, and included representatives of EPA and the California Air Resources Board as participating observers.

With the start of the CRC program, the EPA removed its requirement for the inclusion of MMT in certification fuel, pending completion of these tests. Also, in August of 1977, Congress passed and the President signed into law the Clean Air Act Amendments of 1977. These amendments included a ban of gasoline additives introduced after 1975 unless the EPA Administrator waived this prohibition under Section 211 of the Act. This ban was to be effective on September 15, 1978. Thus, the CRC program was aimed at providing both industries and the EPA with sound technical information upon which to judge the merits of the continued use of MMT. Ethyl Corporation, the sole manufacturer of MMT, applied for such a waiver in March of 1978.

To review all available data, EPA held a Public Hearing in June of 1978 on the Ethyl request. Although the CRC test was incomplete at that time, preliminary information obtained during 22 500 (22.5K) miles of testing was presented at the Public Hearing. In September 1978, the EPA Administrator rejected Ethyl's waiver request and a ban on the use of MMT in unleaded gasoline went into effect in October of 1978.

This paper presents the final results of the CRC program, which was probably the largest and most comprehensive test of its kind ever attempted. The program involved 63 cars which accumulated over 3 million miles. The primary objective was to determine the effect, relative to clear fuel, of MMT at two different concentration levels on exhaust hydrocarbon emissions. Secondary objectives were to determine MMT effects on catalytic converter plugging, catalyst conversion efficiency, oxygen sensor life, and spark plug life. All exhaust emission tests were conducted by Systems Control, Inc. (SCI)--formerly Olson Laboratories--and the cars accumulated mileage at the Riverside International Raceway (RIR) under contract with SCI (6). A complete record of test details, experimental results, and data analysis can be obtained from the Coordinating Research Council (7).

EXPERIMENTAL PROGRAM

Because of the importance to both industries and the Nation of the continued use of MMT, it was recognized at the outset that the accuracy and precision of the test results were critical to the program's goal. Small differences in already low exhaust emission levels would have to be determined with high statistical confidence. After consultation and review with the EPA, a fleet of 63 vehicles was chosen. This fleet size was designed to provide a statistically powerful test for detecting MMT-related emissions effects as small as a difference of approximately 0.1 g/mile hydrocarbon after 50K miles and/or a 40 percent difference in regression slopes*. Details of several approaches for estimating fleet size are included in the CRC Report (7).

The test design included the use of three fuels and seven vehicle models, six domestic and one foreign. All vehicles were designed to meet 1977-78 California exhaust emission standards. Three vehicles of each model were tested per fuel, resulting in a total of nine vehicles for each model. To involve the most advanced emission control systems available, two three-way catalyst equipped models were included. The six domestic models were divided among the three major U.S. manufacturers in approximate proportion to market share.

Vehicles selected by the car manufacturers for the fleet were those considered to be sensitive to MMT and/or representative of future large volume products. The vehicle fleet is described in Table 1.

Fuels selected for the program were Indolene clear (HO III) for emission testing and Chevron certification fuel for mileage accumulation. The Chevron fuel was tested clear (0 MMT), with 1/32 g Mn/gal (1/32 MMT), and with 1/16 g Mn/gal (1/16 MMT). The 1/16 MMT level was selected because that was the maximum concentration recommended by Ethyl Corporation at the time this test program was finalized.

Originally, triplicate emission tests were conducted. Later it was decided, based on observed test precision, that duplicate emission tests were adequate at 0.3K, 5K, 10K, 15K, 22.5K, 30K, 37.5K, 45K, and 50K miles. Tests were run according to EPA exhaust emission certification procedures which includes preconditioning prior to emission testing, except that evaporative emission tests were not run. Scheduled maintenance was conducted at the manufacturer-recommended mileage. Emission testing at the maintenance intervals was conducted with each vehicle as received and after maintenance had been performed. Maintenance procedures are discussed in a later section of this paper.

Vehicles accumulated mileage using the EPA driving schedule. Cars were driven a maximum of 19 hours per day. The vehicles were transported by car carriers between the laboratory and the test track, which were 50 miles apart.

An elaborate quality control and data management system was developed at the contracted laboratory, SCI, and at the test track, RIR. Before the program began, several CRC member companies assisted the SCI laboratory in setting up equipment, refining test procedures, and verifying test results to ensure that high quality emission test data would be obtained (6).

*Slope of the regression line for tailpipe HC emissions versus miles.

In addition, CRC hired a resident project manager and two full-time assistants to monitor the program on-site. This three-man staff was responsible only to CRC.

The CRC also formed a Data Analysis Panel composed of member-company representatives with extensive experience in emission measurements and statistical methods. This Panel is responsible for the data analyses included in this paper.

DATA ANALYSIS

ANALYTICAL METHODS - The data analysis was directed primarily at fuel effects on emission levels averaged over the full 50K miles of testing and at fuel effect changes as a function of test mileage.

Two different types of analyses were performed:

- Analysis of variance of emission levels, simultaneously accounting for fuel, mileage, and model effects.
- Regression analysis of emissions levels versus test miles to obtain linear rates of change of emissions with mileage which were subsequently analyzed to estimate fuel effects.

Each of these approaches makes a different use of the observed data base. Detailed descriptions of the analysis methods and the appropriate data sets are given in the CRC report (7).

DATA BASE - A complete listing of data from the 1801 valid Federal Test Procedure (FTP) tests is also given in the CRC Report (7). In this paper, these data are summarized primarily in the form of graphs.

Of the complete set of valid FTP data, only those tests meeting the following criteria were selected for use in the analyses:

1. Data at scheduled test mileages, starting with 0.3K miles.
2. Data after unscheduled maintenance.
3. Data before and after scheduled maintenance.
4. Data not involved in diagnostic checks.

A few sets of data were rejected because of obvious mechanical problems with the vehicles, such as a melted catalyst, a broken piston, or a malfunctioning carburetor.

TEST VARIABILITY - The test variabilities associated with duplicate and triplicate FTP tests and with the car to car differences were found to be within the estimates used in the design of the test program, assuring that the test as conducted was as powerful as originally planned.

Test Repeatability - The overall FTP test repeat error, defined as $\hat{\sigma}$ (repeat) = standard deviation/mean x 100 percent, was 9.0 percent for tailpipe hydrocarbon (TPHC) and 5.2 percent for engine-out hydrocarbon (EOHC), based on over 1 100 degrees of freedom each. The car models differed in their test repeatability for TPHC, falling into three groups as shown in Table 2.

The engine-out HC precision shown in Table 2 does not exhibit any such strong grouping and does not correlate with the tailpipe precisions.

Car-Mileage Error - The car x mile error term from this program, $\hat{\sigma}$ (car x miles), was 0.073 g/mile for tailpipe HC, giving 0.20×10^{-5} g/mile/mile as the error for the difference between HC slope values for two fuels. These are slightly higher than, but within the uncertainty of the original estimates (0.056 g/mile and 0.15×10^{-5} g/mile/mile) used to design the program (7).

The several car models form two definite groups with respect to the magnitude of this TPHC car x miles error term as shown in Table 3.

The original estimate of 0.056 g/mile is between the values found for the low and high error groups. No such groupings were found for the other emission constituents.

EXHAUST EMISSIONS

Exhaust emissions of hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NO_x) were measured simultaneously at the engine ahead of the catalytic converter (engine-out) and at the tailpipe. Catalytic converter efficiencies were calculated from engine-out and tailpipe emission measurements. The effect of MMT on each of these emission constituents will be discussed in the following sections. For this discussion, data have been separated into three categories: 1) all car data; 2) data from all cars with conventional oxidation catalysts (COC) which includes the Buick Century, Oldsmobile Cutlass, Ford Granada, Ford LTD, and Plymouth Volare; and 3) data from cars with three-way catalysts (TWC) which includes the Pontiac Sunbirds and Volvos.

TAILPIPE HC EMISSIONS - Plots of tailpipe HC emissions from all cars, COC cars, and TWC cars are shown in Figures 1, 2, and 3, respectively. From these figures it is apparent that tailpipe HC emissions from the clear-fueled cars were consistently lower than emissions from the corresponding MMT-fueled cars throughout the 50K mile test. Furthermore, emissions with 1/32 MMT fuel were usually somewhat lower than those with 1/16 MMT fuel.

Another way to look at fuel effects is to plot the difference in tailpipe HC between MMT fuel and clear fuel at each mileage interval for each car group as is shown in Figures 4, 5, and 6. The MMT fuels averaged consistently higher tailpipe HC levels than did the clear fuel. As shown in Figure 4, the differences in emissions for MMT fuels compared to clear fuel increased linearly for the first 15K miles and then remained relatively constant at about 0.1 g/mile through 50K miles. At 15K miles the differences in tailpipe HC emissions for 1/32 MMT compared to clear fuel was 0.09 g/mile and the difference for 1/16 MMT compared to clear fuel was 0.12 g/mile. Corresponding differences at 50K miles were 0.09 g/mile and 0.11 g/mile. These differences are all significant at levels above 95 percent.

The COC cars showed the same general pattern as the all-car results as shown in Figure 5. The difference in the tailpipe hydrocarbon emissions for the MMT fuels versus clear fuel increased through 15K miles and then leveled off at about 0.1 g/mile through 50K miles.

The TWC cars also showed the same general patterns as the all-car results, except that there was a substantial peak at 30K miles (Figure 6). This peak is due to high emissions before the oxygen sensor change at scheduled maintenance.

The tailpipe HC data were analyzed using analysis of variance techniques, the details of which can be found in the CRC Report (7). From this analysis it was determined that fuel effects (higher tailpipe HC emissions with MMT fuel) were significant at levels greater than 95 percent.

These data were also analyzed by linear regressions of tailpipe HC emissions versus miles. Average regression slopes for each car model and for all cars on each fuel are summarized in Table 4. The 1/32 MMT mean slope is 41 percent greater than that for clear fuel over the 0.3K to 50K mile range. For the 1/16 MMT fuel, the mean slope is 45 percent greater than that for clear fuel for 0.3K to 50K miles. The MMT effect on regression slopes was significant at a level greater than 95 percent.

Another method of analyzing the tailpipe HC data is to determine the mileage at which the emissions first exceed the California legislated standard of 0.41 g/mile (violation mileage). Tailpipe HC emissions were adjusted for the methane allowance permitted by California, averaged for each car model, and compared to the California standard. The results are shown in the bar graph of Figure 7. A nonparametric analysis of variance showed that the average violation mileages for the clear-fueled cars are highest, the 1/32 MMT-fueled cars are next highest, and the 1/16 MMT-fueled cars are lowest. The significance levels were 88 percent for the separation between clear and 1/32 MMT fuels, 97 percent for the separation between 1/32 MMT and 1/16 MMT fuels, and 99 percent for the separation between clear and 1/16 MMT fuels.

ENGINE-OUT HC EMISSIONS - Figures 8, 9, and 10 show the engine-out hydrocarbon (EOHC) emission averages for all cars on each fuel, all COC cars on each fuel, and all TWC cars on each fuel. The emissions with 1/32 MMT fuel are approximately midway between those with clear fuel and 1/16 MMT fuel in the 30K to 50K mile range. This probably corresponds to the mileage range for which engine deposits have stabilized.

The differences in EOHC between MMT fuels and clear fuel are plotted in Figures 11, 12, and 13 for the three different car categories. For all cars (Figure 11), the fuel differences show a rapid rise up to 15K miles after which the 1/16 MMT fuel difference continues to rise somewhat more slowly to about 0.7 g/mile from 30K to 50K miles, while the 1/32 MMT fuel difference levels out at about 0.4 g/mile above clear fuel for the duration of the test. The differences at 50K miles were 0.48 g/mile for 1/32 MMT versus clear fuel and 0.79 g/mile for 1/16 MMT versus clear fuel. The COC cars (Figure 12) show the same basic trends: a rapid rise above clear fuel up to 15K miles with fairly constant differences from clear fuel between 30K and 50K miles. The TWC cars (Figure 13) show the same trends as the other cars.

The EOHC data were analyzed using an analysis of variance, and the MMT fuel effects were significant above the 90 percent level. In addition, it was determined that EOHC increased linearly with MMT concentration in the fuel.

The EOHC data in the 30K to 50K mile range were regressed against engine-out CO (EOCO) and mileage as independent variables. Averaged EOCO was used because this is not affected by MMT in the fuel as will be discussed later. This is a method of correcting for carburetor differences between individual cars as reflected by EOCO. A regression equation was then obtained with 30K to 50K mile range data for each model and each fuel. These equations represent the best fit of the data over this mileage and can be used to calculate a "best estimate" for a specific mileage and EOCO value. Table 5 shows the "best estimates" of engine-out HC at 50K miles using the average EOCO value for all cars of that model at 50K miles. From Table 5, EOHC are essentially linear with MMT concentration except for the Volares and Volvos. Table 5 also shows the levels of significance at which MMT fuel regression slopes minus clear fuel regression slopes are different from zero. The consistently high levels indicate that both MMT fuels significantly increased EOHC emissions for all models.

HYDROCARBON CATALYTIC CONVERTER EFFICIENCY - Figures 14, 15, and 16 show the hydrocarbon catalytic converter efficiency averages for all cars on each fuel, all COC cars on each fuel, and all TWC cars on each fuel. There is an indication that catalytic converter efficiencies with MMT fuels tend to be somewhat higher than for clear fuel at the high mileages.

Regression analyses similar to those for EOHC were performed for HC catalytic converter efficiencies over the 30K to 50K mile range. This range was selected because efficiencies appear to have stabilized. Efficiencies were regressed against miles as well as EOCO and EOHC (to represent feed gas conditions to the converter). "Best estimates" at 50K miles were calculated with the average value of EOCO for all cars of each model and the 50K-mile EOHC average for each fuel. These are shown in Table 6. Higher converter efficiencies are observed with MMT for all models and fuels except the 1/32 MMT Granadas and Volvos. Analysis for significance shows that the differences between MMT and clear fuel are all different from zero at the 95 percent or higher level.

After completion of the program, the AC Spark Plug Division of General Motors determined hot stabilized efficiency and the time to achieve 50 percent conversion for the catalytic converters from the Buicks, Oldsmobiles, and Pontiacs. These are laboratory tests (8) whereby converter performance is evaluated using an exhaust feedstream of constant HC and CO composition. Table 7 shows the results for stabilized efficiency. Higher efficiencies were observed with the MMT fuels. Results from the tests for time to achieve 50 percent conversion showed no difference between the fuels.

The results from the regression analysis and the AC tests show an increase in catalytic converter efficiency for HC whenever MMT was used in the fuel with the Buicks, Oldsmobiles, and Pontiacs. Converters from the other car models were not checked in similar laboratory tests at the end of the 50K mile program.

CO AND NO_x EMISSIONS - Tailpipe emissions of CO are plotted in Figure 17 for all cars, COC cars, and TWC cars. Both tailpipe and engine-out CO data were analyzed using an analysis of variance, and no significant fuel effects were found. Also, MMT did not significantly affect CO converter efficiency.

Similarly, tailpipe NO_x emissions are plotted in Figure 18; no significant fuel effects were found. Furthermore, MMT did not affect NO_x converter efficiency with the TWC cars.

INSTANTANEOUS EFFECT OF MMT ON EMISSIONS - To evaluate instantaneous MMT effects, the MMT cars were tested for emissions with MMT-spiked Indolene test fuel as well as with clear Indolene, at 0.3K and 22.5K miles. The 1/32 MMT-fueled cars were tested with 1/32 MMT-spiked Indolene; the 1/16 MMT-fueled cars with 1/16 MMT-spiked Indolene.

Thirty cars were tested at 0.3K miles and 36 (all MMT cars except the Granadas) at 22.5K miles. The results are summarized in Table 8. No consistent instantaneous MMT effects were found. Even the statistically significant engine-out effect for the 1/16 MMT tests represents an increase of less than 4 percent.

OTHER OBSERVATIONS

In addition to exhaust emissions, data for vehicle maintenance, oxygen sensor performance, catalytic converter plugging, fuel economy, and oil consumption were also analyzed. Results are discussed briefly in the following sections.

SCHEDULED VEHICLE MAINTENANCE - The manufacturer's recommended maintenance schedule was followed for all vehicles in the fleet. Scheduled maintenance consisted of such items as:

- Spark plug changes.
- Camshaft/valve adjustment.
- Fuel filter replacement.
- Carburetor adjustment.
- PCV system checks.
- Air filter replacement.

Maintenance intervals among the models varied as follows:

Buick, Oldsmobile,
Ford LTD, Plymouth.....30K miles
Ford Granada...........22.5K and 45K miles
Pontiac and Volvo......15K, 30K, 45K
(includes O_2 sensor replacement)

An analysis of variance was performed on the effect of scheduled maintenance on emissions. The effect of this maintenance was insignificant both for the overall effect and specifically for fuel effects. The effect of scheduled oxygen sensor replacement on the Pontiacs and Volvos is discussed later.

UNSCHEDULED VEHICLE MAINTENANCE - Several unscheduled emission-related mechanical repairs and adjustments were made throughout the test. Unscheduled emissions-related maintenance was any adjustment, repair, or part replacement which could affect exhaust emissions and which was not included in scheduled maintenance. Typical problems involved carburetor replacement, resetting idle A/F ratios, and choke adjustments. These repairs were made because it was recognized that these factors could substantially affect exhaust emissions and potentially mask any effect of MMT. Therefore, to minimize test variability, spark timing, idle speed, and mixture ratio were checked and adjusted, if necessary, before each test. In addition, unscheduled maintenance was performed whenever inspections or emission tests indicated a problem.

The unscheduled maintenance data show that the maintenance performed affected HC and CO emissions sometimes resulting in effects larger than those found from fuel differences. These results indicate that the repairs and adjustments were necessary to isolate the effect of MMT.

OXYGEN SENSOR PERFORMANCE - Oxygen sensors were replaced at 15K, 30K, and 45K miles on the TWC vehicles (Pontiacs and Volvos). Also, if unusually high CO emissions were noted at any of the emission check mileages, the oxygen sensor was replaced.

All of the Pontiac sensors and eight sensors from the Volvos were returned to the manufacturers for inspection. For the Pontiacs, one clear fuel, six 1/32 MMT, and four 1/16 MMT sensors were reported as failed. In every case when a sensor failed, CO and HC emissions decreased markedly after a new sensor was installed. The Pontiac sensor data were analyzed using a sign test (counting failures and non-failures), and it can be concluded at the 90 percent confidence level that MMT had an adverse effect on Pontiac sensor life. No conclusion can be drawn from the data on Volvo sensor life, since two sensors showed decreased performance with 1/32 MMT fuel but none with 1/16 MMT fuel. However, both the tailpipe HC and CO emissions from the Volvos with MMT fuels decreased after oxygen sensor changes.

CATALYTIC CONVERTER PLUGGING - A secondary objective of the MMT fleet test program was to determine whether the combustion products from MMT fuels plug catalysts. A simple test procedure was devised whereby the pressure drop (ΔP) across the catalyst was measured during a wide-open throttle acceleration from 0 mph to 50 mph. The ΔP was monitored by a differential pressure gage, and the maximum ΔP was recorded. In most cases, the maximum ΔP occurred at the transmission shift point from first to second gear at about 30 mph to 35 mph.

Analysis of the data showed no differences in pressure drop between the fuels. There was no indication of catalyst plugging with any of the fuels.

FUEL ECONOMY - Throughout the 50K-mile test, fuel economy was monitored at various mileages by two methods: the 1975 FTP using the carbon balance measurement concurrent with emissions testing, and direct track mileage measurement versus fuel consumed. No effect of MMT on fuel economy was noted with either method.

OIL CONSUMPTION - The oil consumption for all 63 cars was monitored over the 50K mile test. Oil consumption rates were computed by taking the quarts of oil added (including oil changes and makeup oil) minus the quarts of oil drained and dividing by the miles accumulated in the test interval. The oil consumption for each car model was obtained by averaging the individual car results according to fuel type.

The data (7) showed that oil consumption varied markedly from one car model to another. However, there is no indication with any of the models that fuel type has an effect on the amount of oil consumed.

CONCLUSIONS

The data from the 63-car fleet test were analyzed several different ways. The major conclusions based on these analyses are as follows:

1. Both 1/32 MMT and 1/16 MMT fuels increased tailpipe hydrocarbon emissions in comparison to the clear fuel as summarized in Table 9. At 50K miles, the average increase was 0.09 g/mile HC for 1/32 MMT fuel, and 0.11 g/mile HC for 1/16 MMT fuel. This increase was most pronounced at 15K miles, and significant differences between MMT-fuel and clear-fuel tailpipe hydrocarbons continued for the duration of the test.

2. For four car models, MMT at either concentration significantly reduced the mileage at which tailpipe hydrocarbon emissions first exceed the California emission standard of 0.41 g/mile.

3. Engine-out hydrocarbons increased with the MMT fuels, and that increase was proportional to the MMT concentration in the fuel. The average differences for all car models at 50K miles, relative to clear fuel, were 0.48 g/mile for 1/32 MMT fuel and 0.79 g/mile for 1/16 MMT fuel. These differences were significant above the 90 percent confidence level.

4. MMT had no effect on tailpipe or engine-out CO and NO_x for all cars throughout the 50K-mile test.

5. The catalytic converter efficiency for hydrocarbons was 2 to 3 percent higher with the MMT fuels than with clear fuel for all cars at 50K miles. However, the increased converter efficiencies with MMT were not sufficient to compensate for the increase in engine-out hydrocarbons at the MMT concentrations used in this test. MMT did not affect converter efficiency for CO with all cars or for NO_x with the TWC cars.

6. Emission tests with MMT-spiked Indolene showed no instantaneous effect on tailpipe or engine-out hydrocarbons compared to Indolene without MMT.

7. MMT affected the oxygen sensors of two car models equipped with TWC systems. With the Pontiacs, MMT fuels at either level decreased the life of the oxygen sensor, resulting in a marked increase in tailpipe hydrocarbon and carbon monoxide emissions. With the Volvos, both the tailpipe hydrocarbons and carbon monoxide emissions with MMT fuels decreased after oxygen sensor changes.

8. Manufacturer's recommended scheduled maintenance, including spark plug changes, had no discernible effect on emissions with any fuels. Spark timing and idle adjustments were checked before each emissions test and various mechanical repairs were made whenever needed throughout the 50K-mile test. These unscheduled repairs were made since mechanical malfunctions could substantially affect exhaust emissions independent of fuel type, and thus mask an assessment of any MMT effect.

9. Catalyst pressure drop measurements indicated no instances of catalyst plugging with any fuel.

10. Oil consumption and fuel economy data indicated no detectable MMT effect.

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Table 1 - Description of Test Vehicles

Model Year	Total No. Vehicles	Vehicles	Engine Size, Cu. In.	Config.	Inertia Weight, Lb.	Type of Emission Controls*
1977	9	Buick Century	231	V-6	4 000	AIR, COC, EGR
1977	9	Olds Cutlass	350	V-8	4 500	AIR, COC, EGR
1978	9	Pontiac Sunbird	151	L-4	3 000	TWC, EGR
1978	9	Ford Granada	302	V-8	3 500	AIR, COC, EGR
1978	9	Ford LTD II	351	V-8	4 500	AIR, COC, EGR
1977	9	Plymouth Volare	225	L-6	4 000	AIR, COC, EGR
1977	9	Volvo 242	130	L-4	3 000	TWC, EFI

* AIR = Air Injection Reactor
COC = Conventional Oxidation Catalyst
EGR = Exhaust Gas Recirculation
TWC = Three-way Catalyst with Oxygen Sensor
EFI = Electronic Fuel Injection

NOTE: All vehicles were designed to meet 1977-78 ~~California~~ emission standards of 0.41 g/mi HC, 9.0 g/mi CO, and 1.5 g/mi NO_x.

Table 2 - Test Repeatability

Model	$\hat{\sigma}$ (Repeat) - % Tailpipe HC		$\hat{\sigma}$ (Repeat) - % Engine-out HC
Pontiac Sunbird	5.2	- Low	4.2
Buick Century	8.5		4.9
Ford Granada	7.1	- Average	6.5
Volvo	8.2		3.8
Ford LTD II	10.4		6.8
Olds Cutlass	10.3	- High	5.0
Plymouth Volare	11.1		4.2
Average	9.0		5.2

Table 3 - Car x Mile Errors - Tailpipe HC

Low Error Group		High Error Group	
Model	$\hat{\sigma}$ (Car x Miles), g/mi	Model	$\hat{\sigma}$ (Car x Miles), g/mi
Buick Century	0.043	Ford Granada	0.090
Ford LTD II	0.039	Plymouth Volare	0.094
Olds Cutlass	0.042	Pontiac Sunbird	0.116
Volvo	0.039		
Average Low	0.041	Average High	0.101

Pooled Average 0.073

Table 4 - Tailpipe Hydrocarbon Regression Slopes
Combined Cars of the Same Model

	Slope for 0.3K to 50K Miles (10^{-5} g/mile/mile)	Seven Car Models Mean	Std. Deviation
0 MMT			
Buick	0.270		
Oldsmobile	0.146		
Pontiac	0.288		
Granada	1.303		
LTD	0.488		
Volare	0.623		
Volvo	0.040	0.450	0.270
1/32 MMT			
Buick	0.433		
Oldsmobile	0.206		
Pontiac	0.354		
Granada	2.093		
LTD	0.324		
Volare	0.864		
Volvo	0.179	0.636	0.205
1/16 MMT			
Buick	0.641		
Oldsmobile	0.312		
Pontiac	0.737		
Granada	1.668		
LTD	0.603		
Volare	0.572		
Volvo	0.027	0.651	0.275

Table 5 - Effect of MMT on Engine-Out Hydrocarbons

Model	Fuel	Best Estimate of EOHC at 50K Miles, g/mile	Significance Level That MMT Fuel EOHC is Different Than Clear Fuel
Buick	Clear	1.476	
	1/32 MMT	1.748	99+
	1/16 MMT	2.076	99+
Oldsmobile	Clear	1.759	
	1/32 MMT	2.050	99+
	1/16 MMT	2.581	99+
Pontiac	Clear	1.484	
	1/32 MMT	2.286	99+
	1/16 MMT	2.407	99+
Granada	Clear	4.410	
	1/32 MMT	5.217	99+
	1/16 MMT	5.699	99+
LTD	Clear	2.103	
	1/32 MMT	2.313	92
	1/16 MMT	3.342	99+
Volare	Clear	2.321	
	1/32 MMT	2.927	99+
	1/16 MMT	2.642	98+
Volvo	Clear	1.018	
	1/32 MMT	1.413	99+
	1/16 MMT	1.291	99+

Table 6 - Effect of MMT on Hydrocarbon Catalytic Converter Efficiency

Make	Fuel	Best Estimate of Efficiency (%) at 50K Miles	Significance Level (%) That MMT Fuel is Different Than Clear Fuel
Buick	Clear	67.2	
	1/32 MMT	71.8	99+
	1/16 MMT	70.3	97
Oldsmobile	Clear	75.5	
	1/32 MMT	79.2	99+
	1/16 MMT	77.9	99+
Pontiac	Clear	73.8	
	1/32 MMT	79.5	99+
	1/16 MMT	77.2	99+
Granada	Clear	79.8	
	1/32 MMT	76.1	99+
	1/16 MMT	81.4	98
LTD	Clear	77.8	
	1/32 MMT	82.0	99+
	1/16 MMT	83.9	99+
Volare	Clear	76.6	
	1/32 MMT	78.1	98
	1/16 MMT	79.8*	99
Volvo	Clear	82.1	95
	1/32 MMT	78.9	98
	1/16 MMT	83.6	98

*Two cars

Table 7 - Summary of AC Laboratory Tests for HC Catalytic Converter Efficiency

Model	Fuel	Hot Stabilized HC Converter Efficiency - % Average	Minimum	Maximum
Buick	Clear	80.7	79.2	82.3
	1/32 MMT	82.0	81.0	83.3
	1/16 MMT	82.3*	82.3	82.3
Oldsmobile	Clear	83.8	83.3	84.3
	1/32 MMT	86.5	86.4	86.7
	1/16 MMT	85.5	85.0	85.7
Pontiac	Clear	80.3	76	84
	1/32 MMT	87.0	84	89
	1/16 MMT	87.7	87	88

*Value for Car 121 (46.9%) rejected as outlier

Table 8 - Instantaneous Effect of MMT on Hydrocarbon Emissions

Test Mileage	MMT in Mileage Accumulation Fuel	No. of Cars	MMT in Indolene Test Fuel	Emission Source	HC Emissions, g/mile	ΔHC	Significant at What Confidence Level?, %
0.3K	1/32 MMT	14	1/32 MMT	Engine	2.79	-0.07	90
			0		2.86		
			1/32 MMT	Tailpipe	0.28	-0.01	10
			0		0.29		
	1/16 MMT	16	1/16 MMT	Engine	2.11	0.02	33
			0		2.09		
			1/16 MMT	Tailpipe	0.30	-0.04	23
			0		0.34		
22.5K	1/32 MMT	18	1/32 MMT	Engine	2.09	-0.05	81
			0		2.14		
			1/32 MMT	Tailpipe	0.41	0.00	13
			0		0.41		
	1/16 MMT	18	1/16 MMT	Engine	2.25	0.07	99
			0		2.18		
			1/16 MMT	Tailpipe	0.46	0.01	74
			0		0.45		

Table 9 - Summary of Differences in Tailpipe Hydrocarbons for All Car Models

	1/32 MMT Minus Clear	1/16 MMT Minus Clear
0.3K to 50K Mile Regression Slopes, %	+41	+45
ΔHC at 15K Miles, g/mile	+0.09	+0.12
ΔHC at 50K Miles, g/mile	+0.09	+0.11

NOTE: All differences are significant at levels greater than 90 percent.

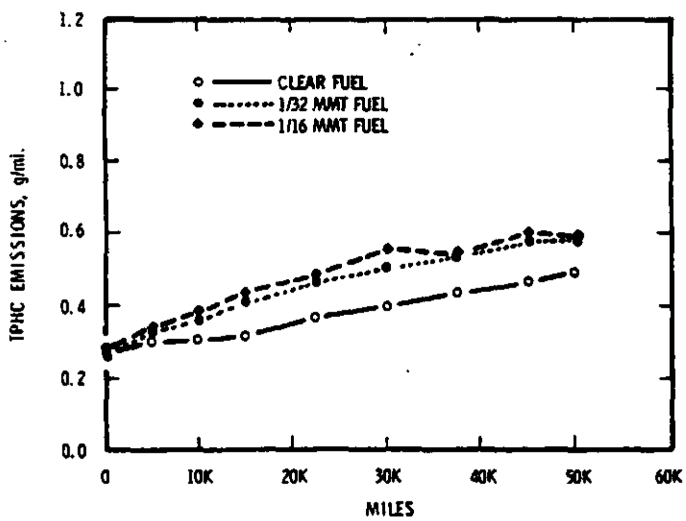

Fig. 1 - Tailpipe hydrocarbon emissions - average for all cars on each fuel

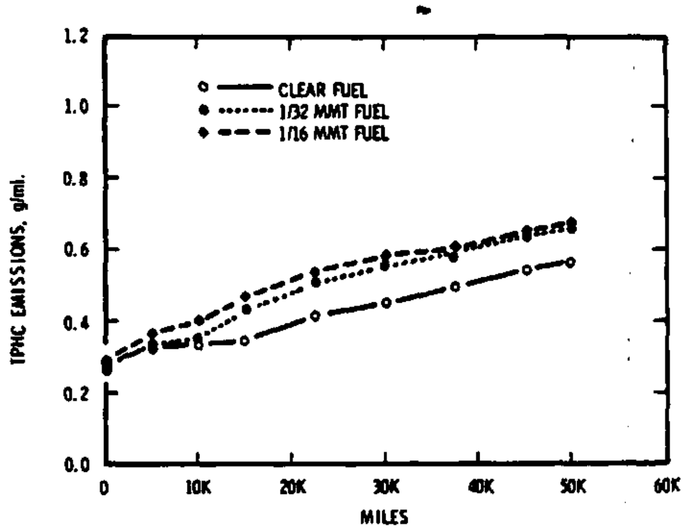

Fig. 2 - Tailpipe hydrocarbon emissions - average for all COC cars on each fuel

Significan at What Confidence Level?, %
90
10
33
23
81
13
99
74

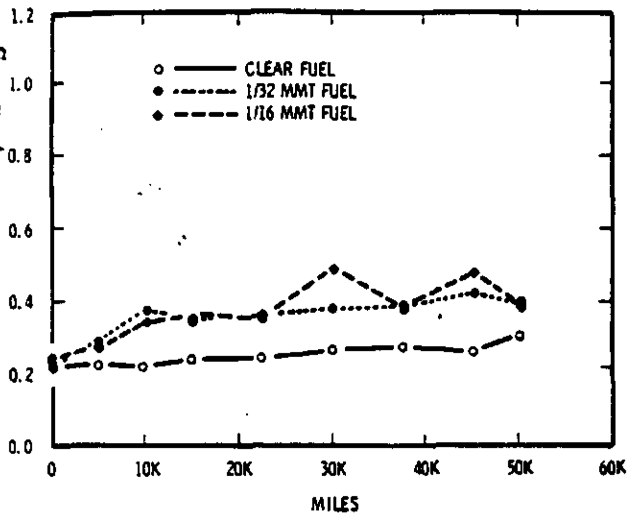

Fig. 3 - Tailpipe hydrocarbon emissions - average for all TWC cars on each fuel

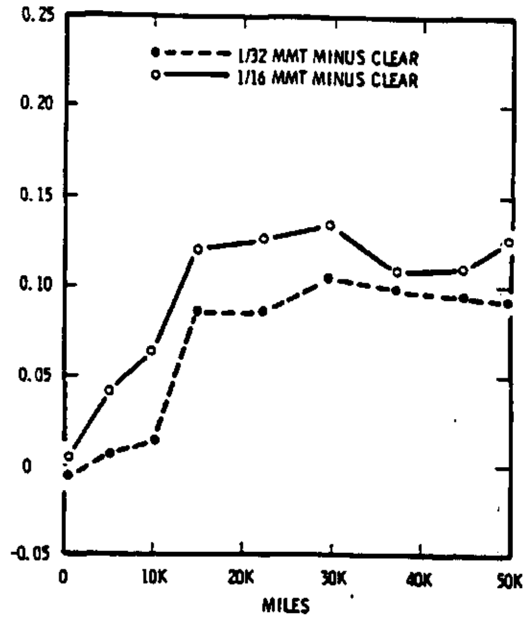

Fig. 5 - Differences in tailpipe hydrocarbon emissions (MMT fuel minus clear fuel) - COC cars

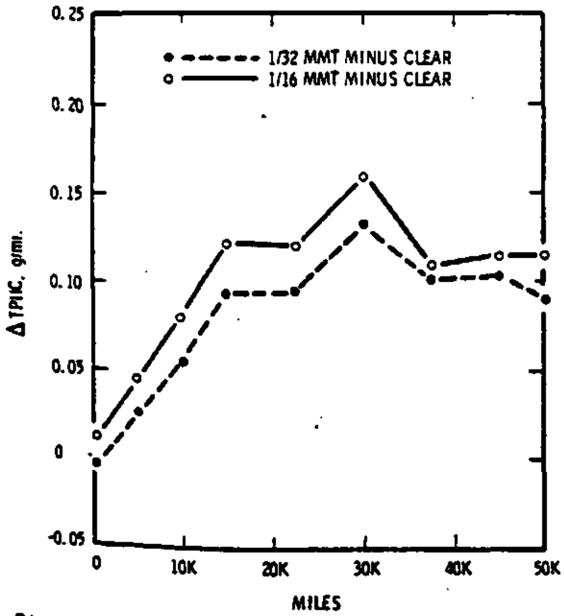

Fig. 4 - Differences in tailpipe hydrocarbon emissions (MMT fuel minus clear fuel) - all cars

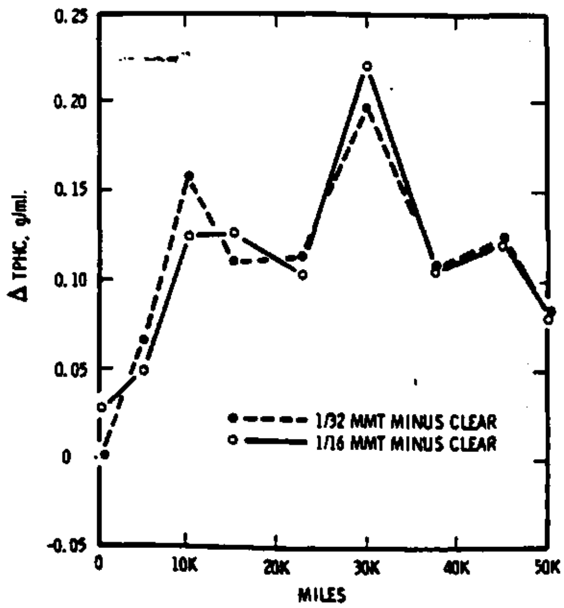

Fig. 6 - Differences in tailpipe hydrocarbon emissions (MMT fuel minus clear fuel) - TWC cars

ons -

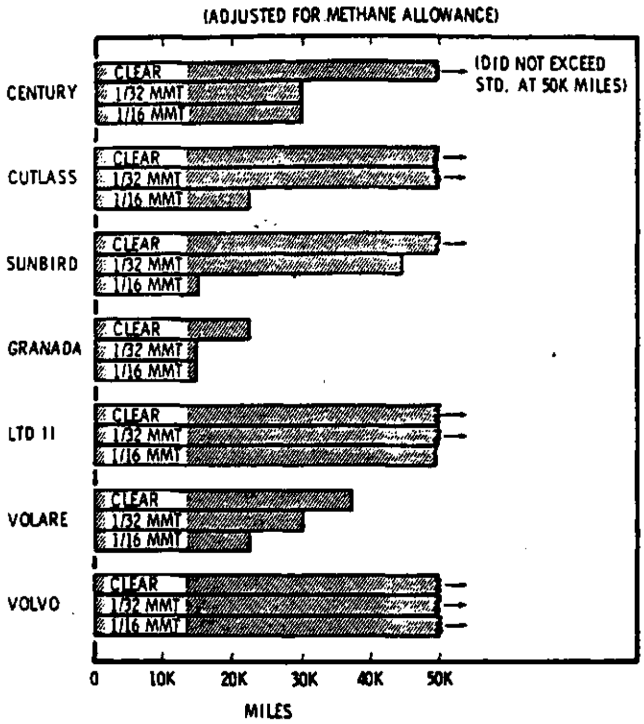

Fig. 7 - Mileage at which tailpipe HC emissions first exceed the California standard of 0.41 g/mi.

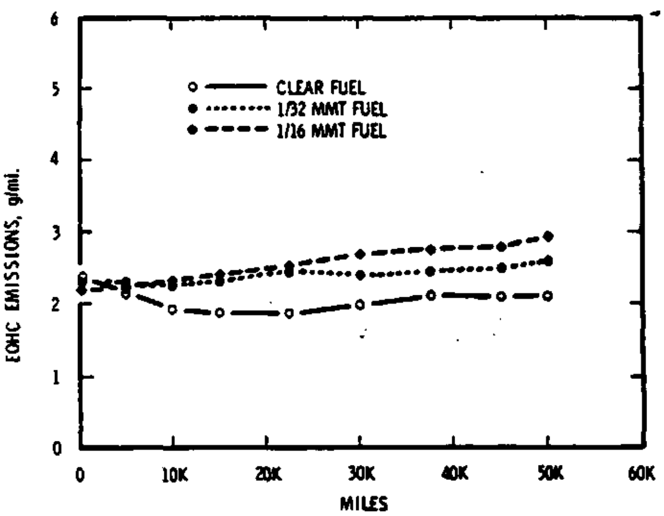

Fig. 8 - Engine-out hydrocarbon emissions - average for all cars on each fuel

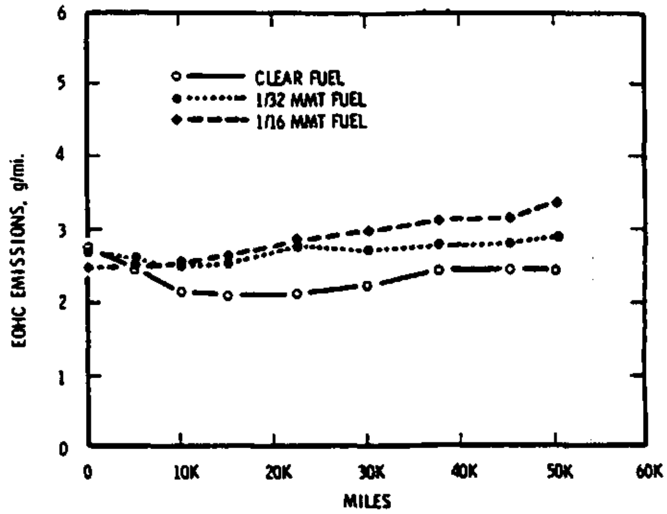

Fig. 9 - Engine-out hydrocarbon emissions - average for all COC cars on each fuel

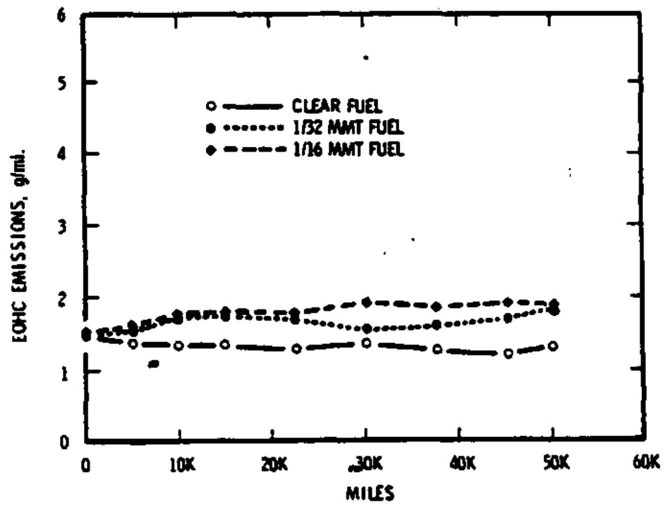

Fig. 10 - Engine-out hydrocarbon emissions - average for all TWC cars on each fuel

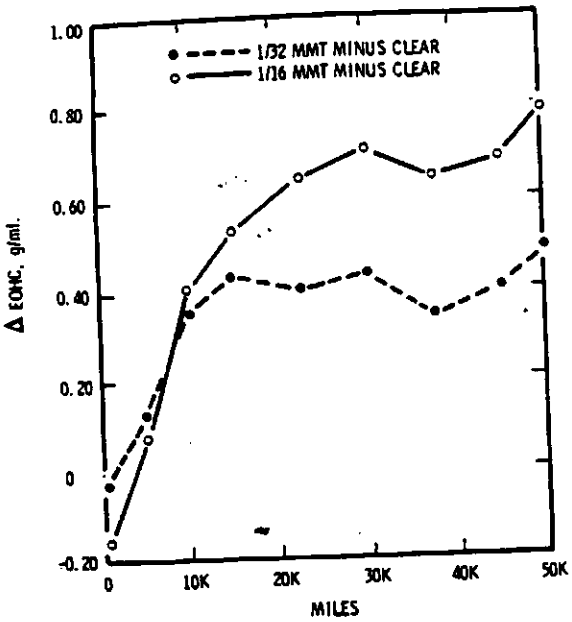

Fig. 11 - Differences in engine-out hydrocarbon emissions (MMT fuel minus clear fuel) - all cars

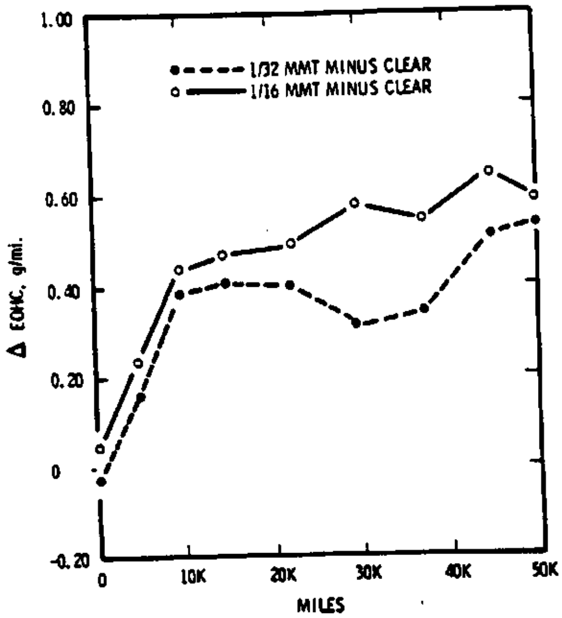

Fig. 13 - Differences in engine-out hydrocarbon emissions (MMT fuel minus clear fuel) - TWC cars

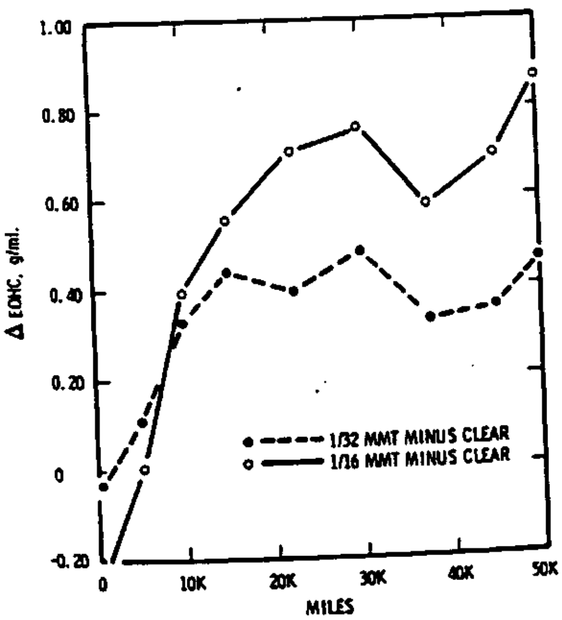

Fig. 12 - Differences in engine-out hydrocarbon emissions (MMT fuel minus clear fuel) - COC cars

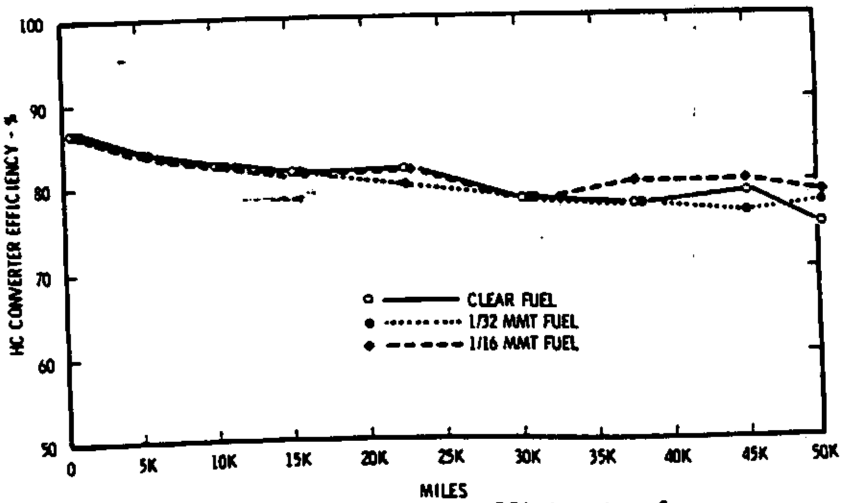

Fig. 14 - Catalytic converter efficiencies for hydrocarbons - average for all cars on each fuel

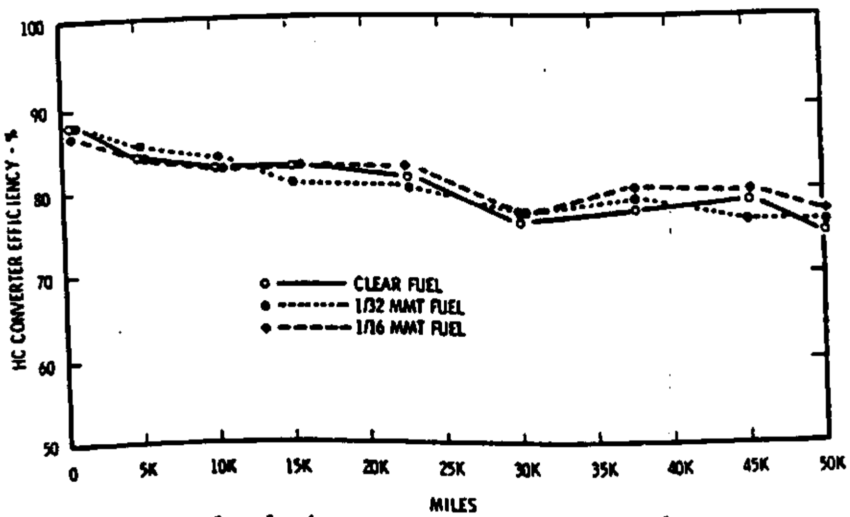

Fig. 15 - Catalytic converter efficiencies for hydrocarbons - average for all COC cars on each fuel

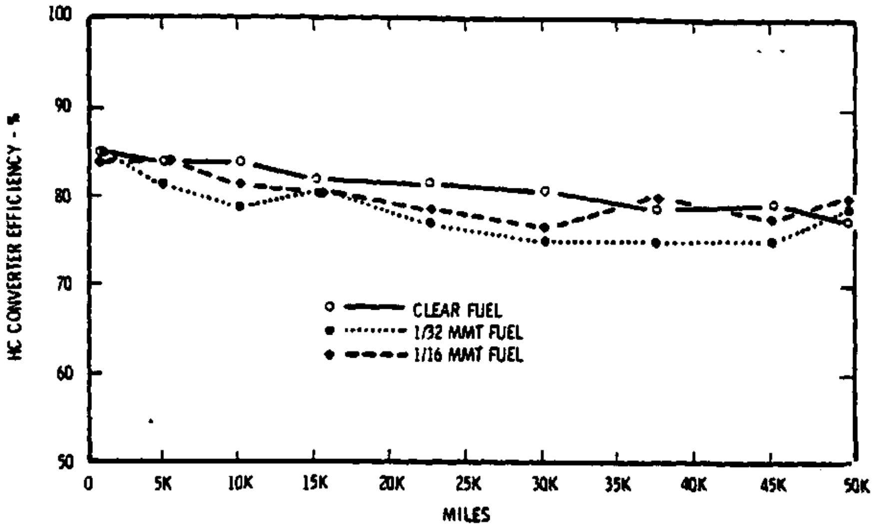

Fig. 16 - Catalytic converter efficiencies for hydrocarbons - average for all TWC cars on each fuel

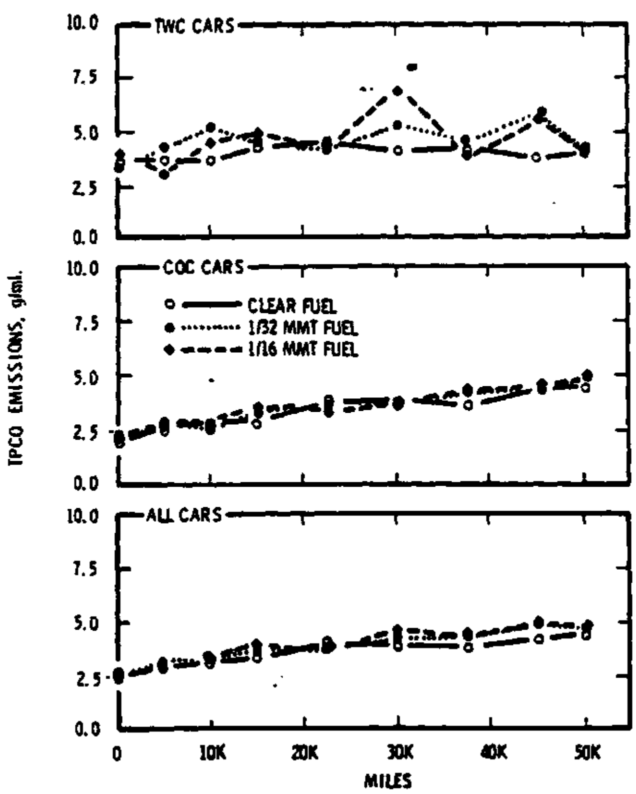

Fig. 17 - Tailpipe carbon monoxide emissions

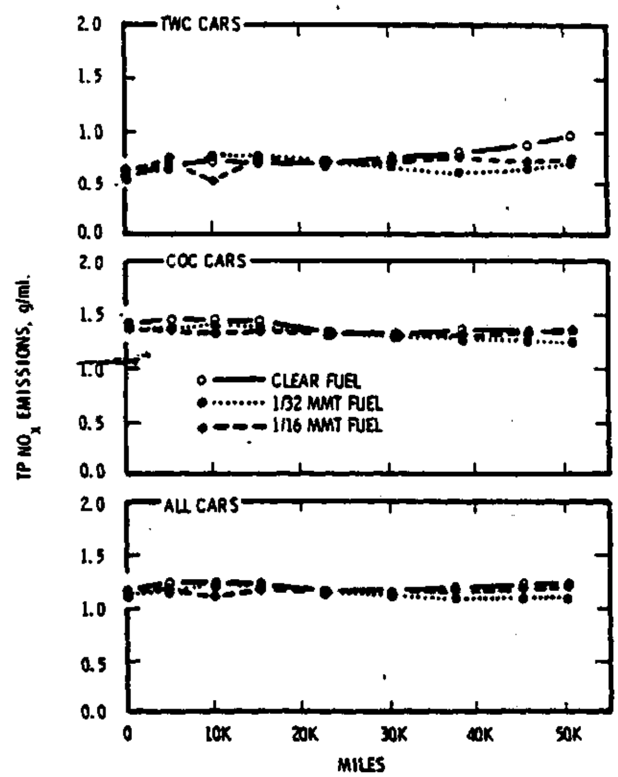

Fig. 18 - Tailpipe nitrogen oxide emissions

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ATTACHMENT 5

DETAILED ANALYSIS OF ETHYL TEST DATA

Note: The following figures and tables were derived from the test data which was provided by Ethyl Corporation on floppy disk. No alterations or deletions were made to the as-received data.

Percent Effect of MMT over Baseline (Averaged Over Range)

Model	Emissions: 0 - 75k miles			Emissions: 0 - 50k miles		
	HC	CO	NOx	HC	CO	NOx
C	21.44	8.77	-27.17	23.60	8.44	-22.32
D	5.62	-2.08	7.61	11.05	1.42	12.40
E	8.28	5.07	-7.11	14.04	12.58	-5.33
F	3.01	-34.61	-26.98	0.27	-29.94	-20.44
G	22.67	2.36	-4.69	23.16	-1.26	-1.62
H	5.79	-3.47	-15.75	4.90	-0.65	-7.78
I	2.57	-7.71	-1.16	-0.05	-9.33	12.52
T	8.51	-1.34	-28.12	12.41	4.79	-30.54
Ave. %Dif	9.74	-4.13	-12.92	11.17	-1.74	-7.89

TABLE 1

Effect of MMT on Engine-Out and Tailpipe Emissions at 50k and 75k

	Engine Out:			Tailpipe:		
	MMT	EEE	MMT vs. EEE	MMT	EEE	MMT vs. EEE
50,000 Miles						
Escort - HC	1.835	1.790	3%	0.207	0.238	-13%
CO	12.317	12.570	-2%	5.779	6.259	-8%
NOx	2.169	2.145	1%	0.454	0.491	-8%
Taurus - HC	2.889	2.556	13%	0.445	0.419	6%
CO	16.325	16.093	1%	5.986	6.245	-4%
NOx	3.467	3.594	-4%	0.666	0.824	-19%
75,000 Miles						
Escort - HC	1.804	1.651	-9%	0.229	0.238	-4%
CO	11.299	11.841	5%	5.651	6.414	-12%
NOx	2.238	2.266	1%	0.432	0.503	-14%
Taurus - HC	2.802	2.442	-15%	0.415	0.385	8%
CO	14.302	14.160	1%	4.976	5.255	-5%
NOx	4.111	4.287	4%	0.646	0.815	-21%

TABLE 2

214

FIGURE 1

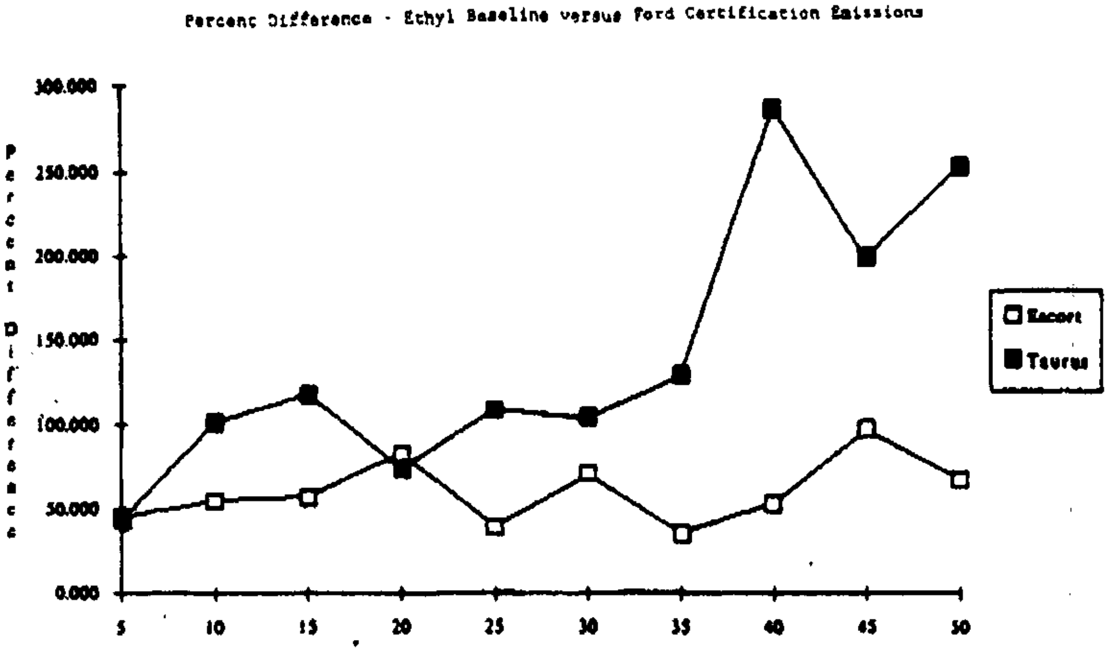


FIGURE 2

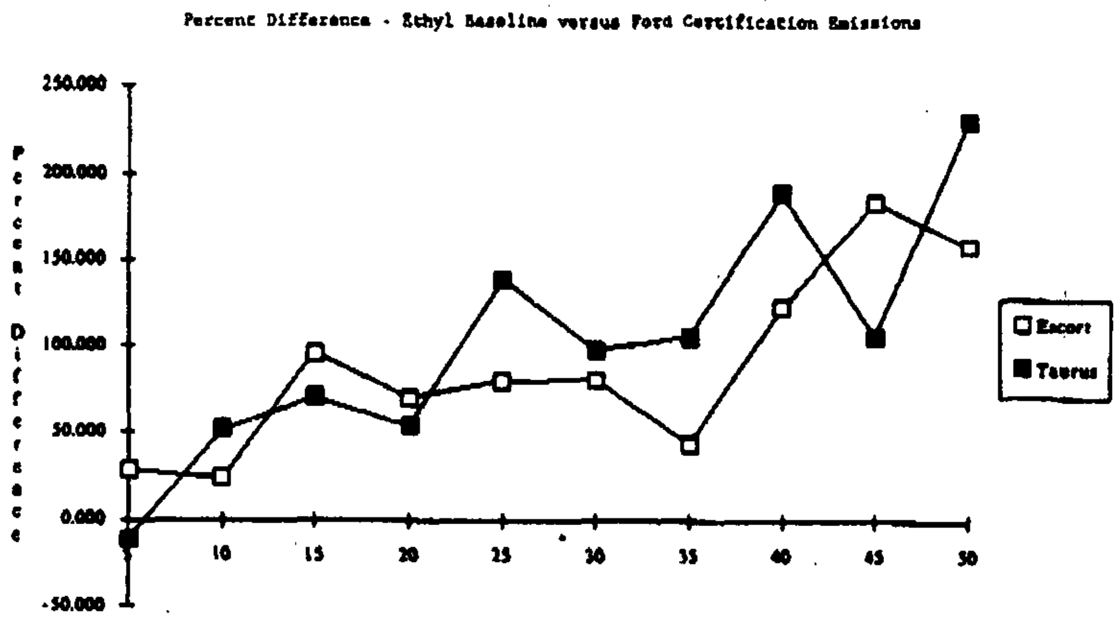
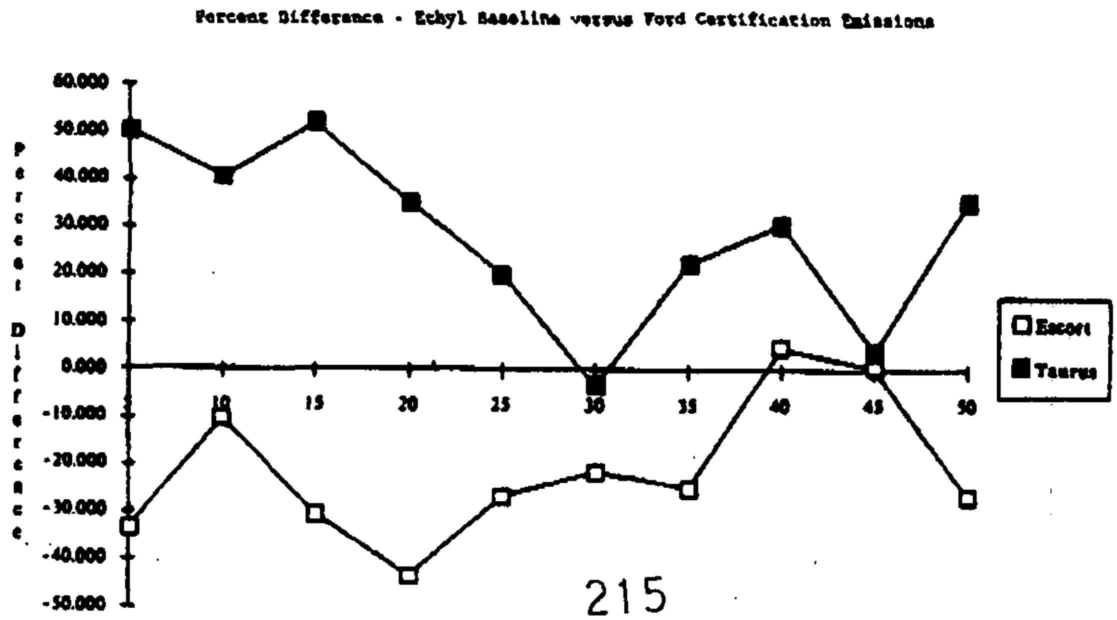


FIGURE 3



Effects of MMT on Vehicle Emissions - Model C

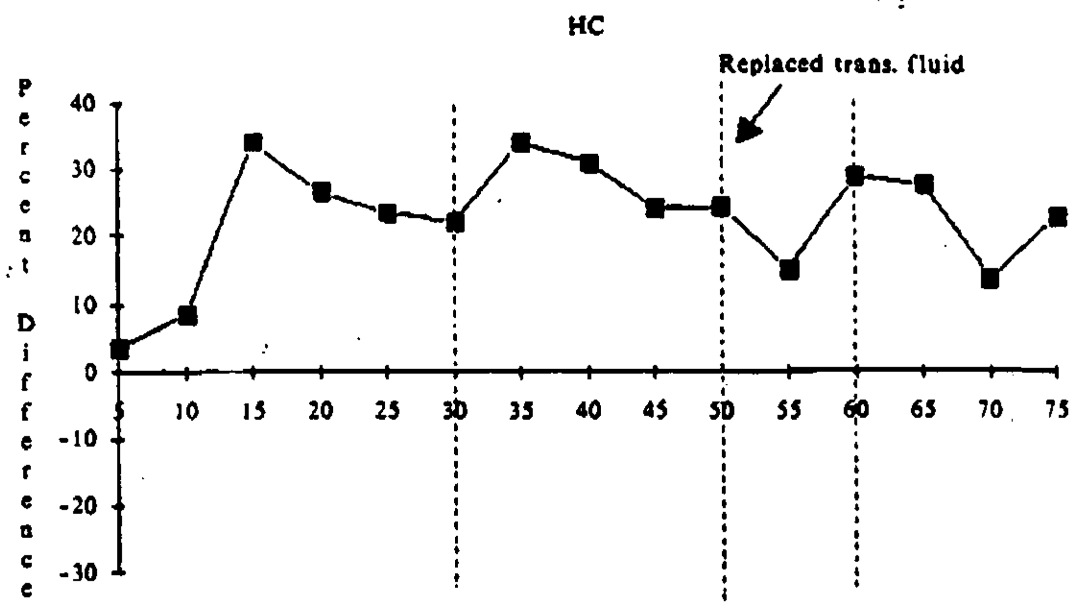


FIGURE 4

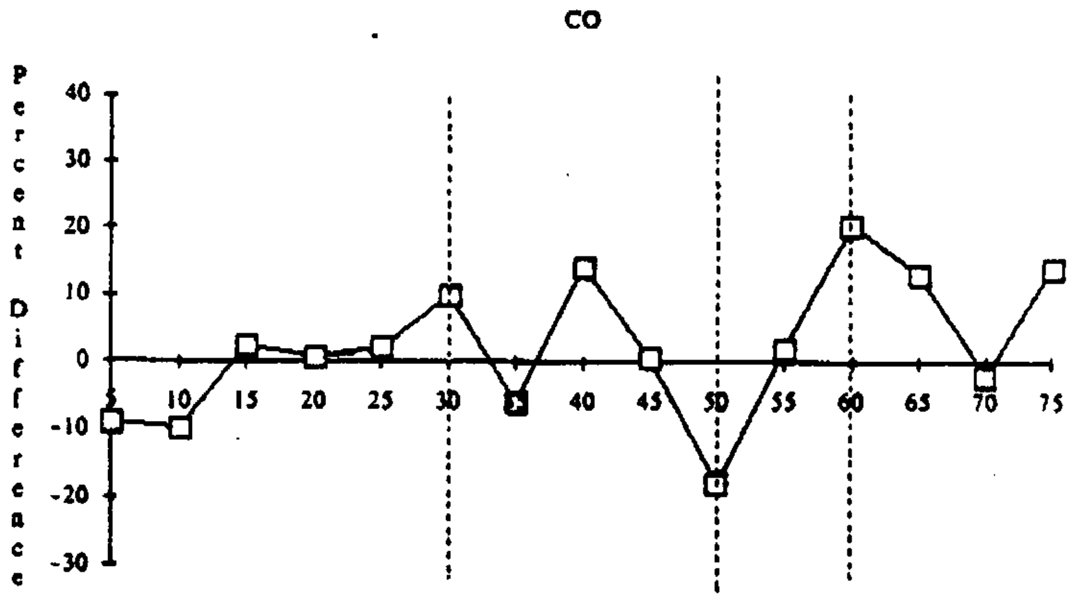


FIGURE 5

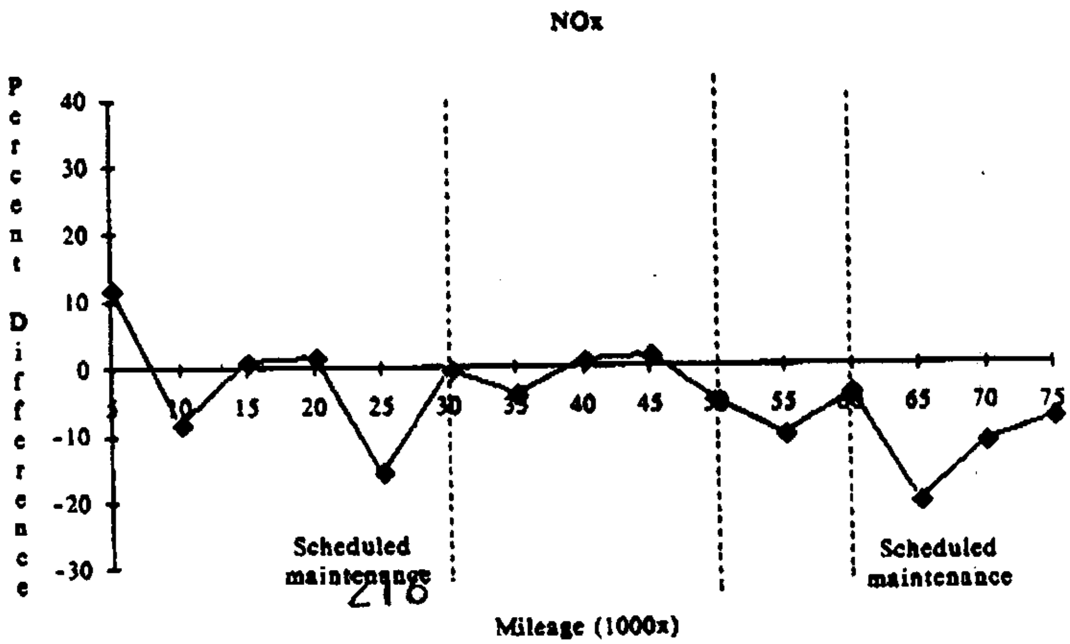


FIGURE 6

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Effect of MMT on Vehicle Emissions - Model "D"

FIGURE 7

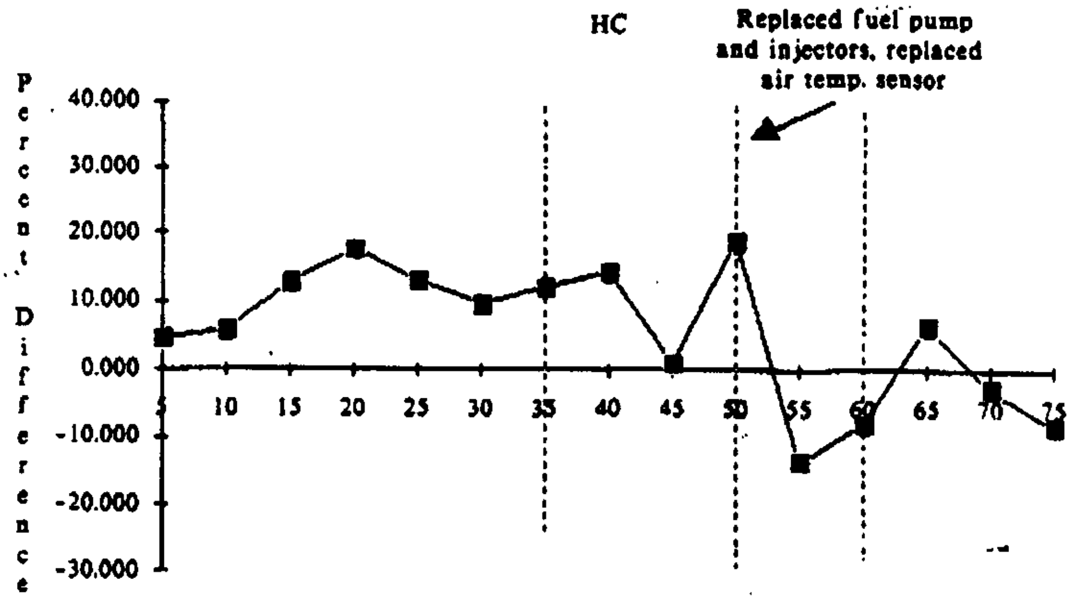


FIGURE 8

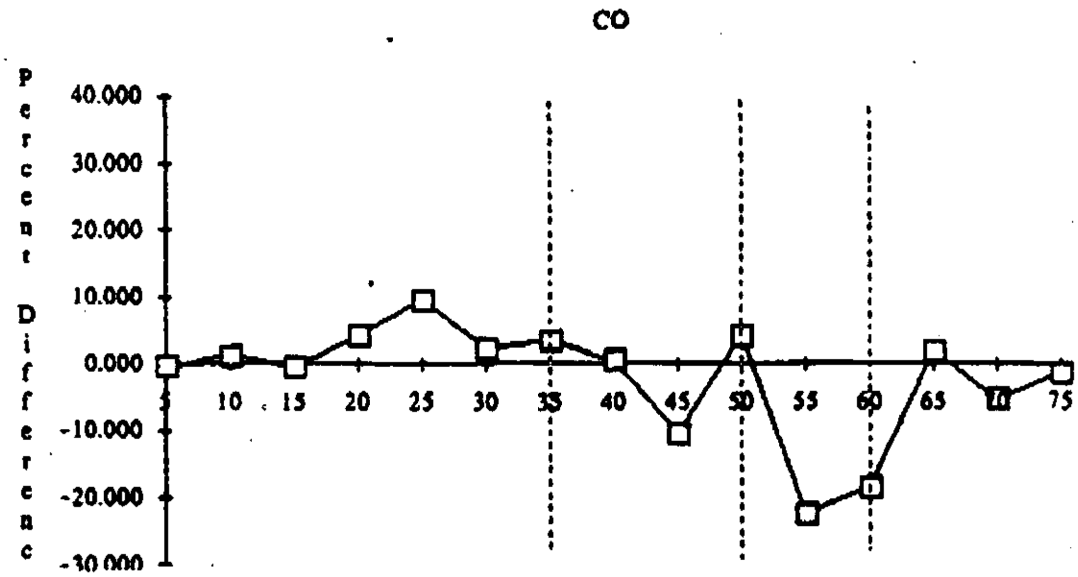
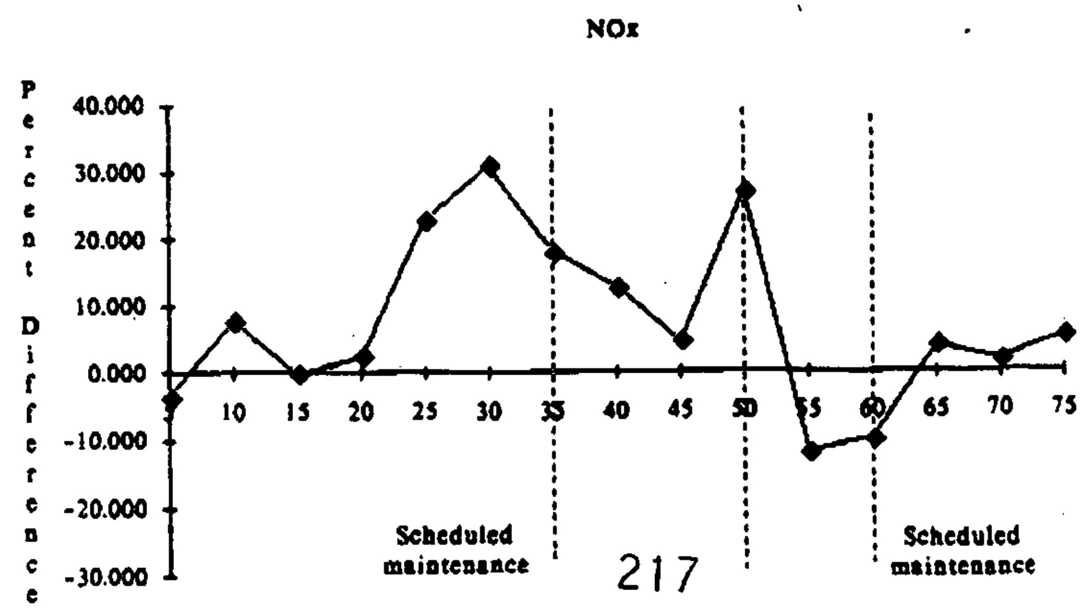
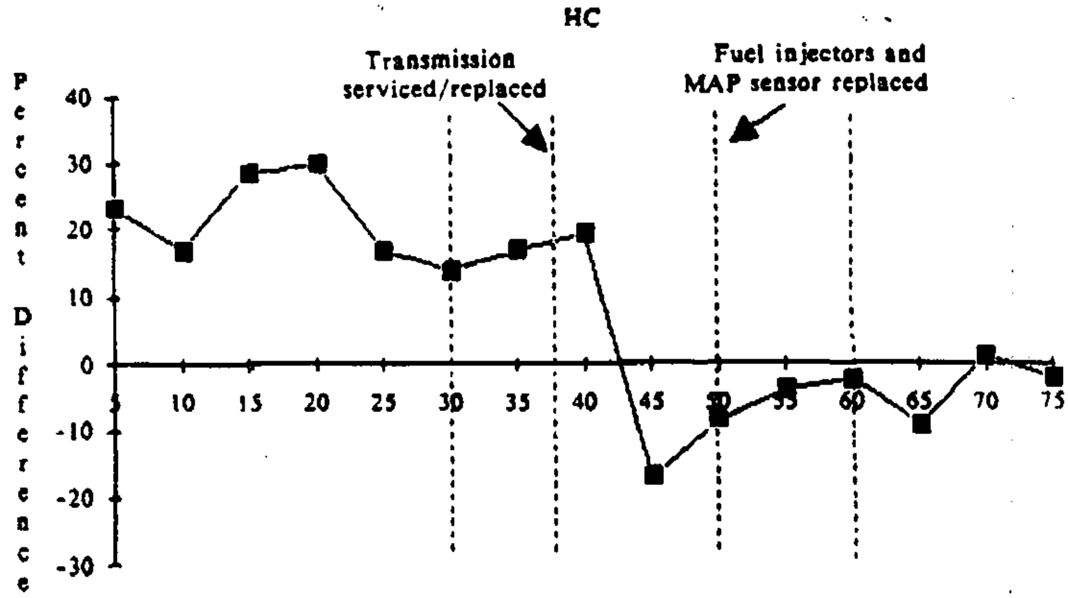


FIGURE 9



Effects of MMT on Vehicle Emissions - Model E

FIGURE 10



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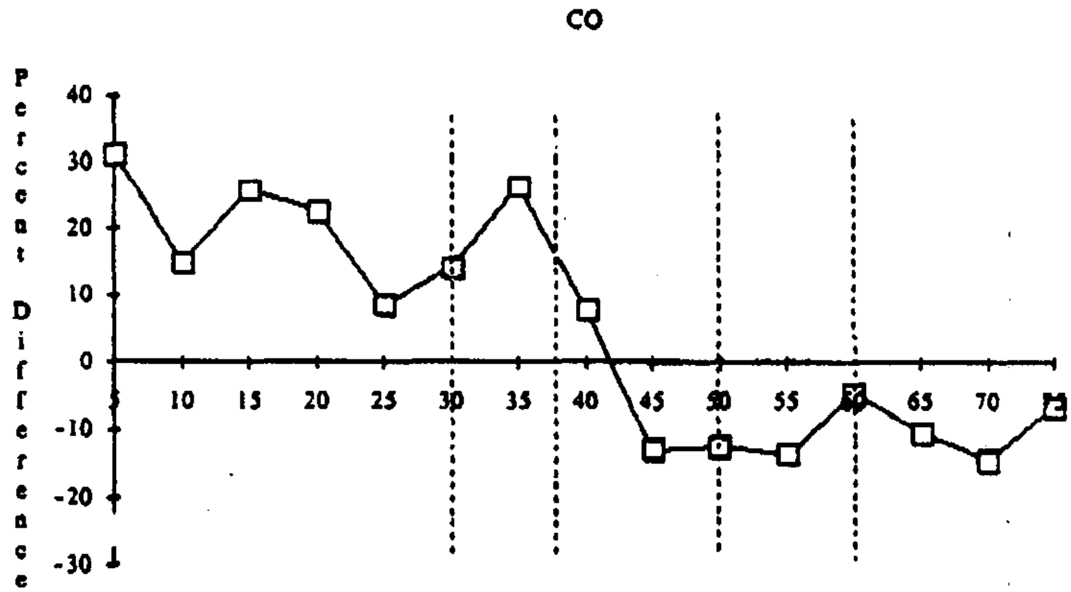
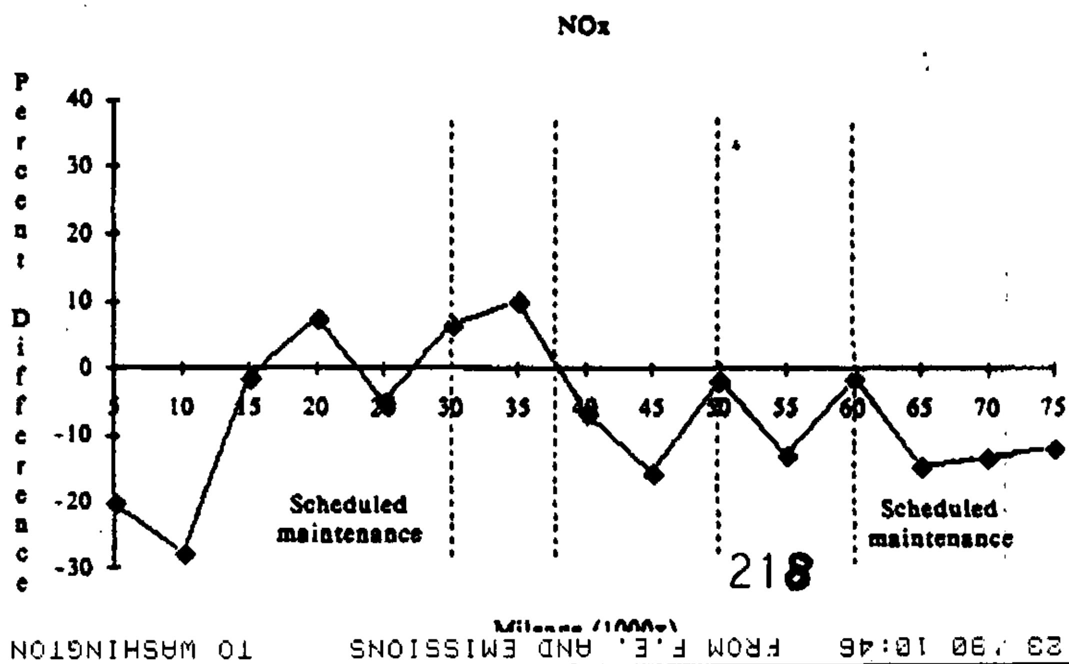


FIGURE 12



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Effects of MMT on Vehicle Emissions - Model F

FIGURE 13

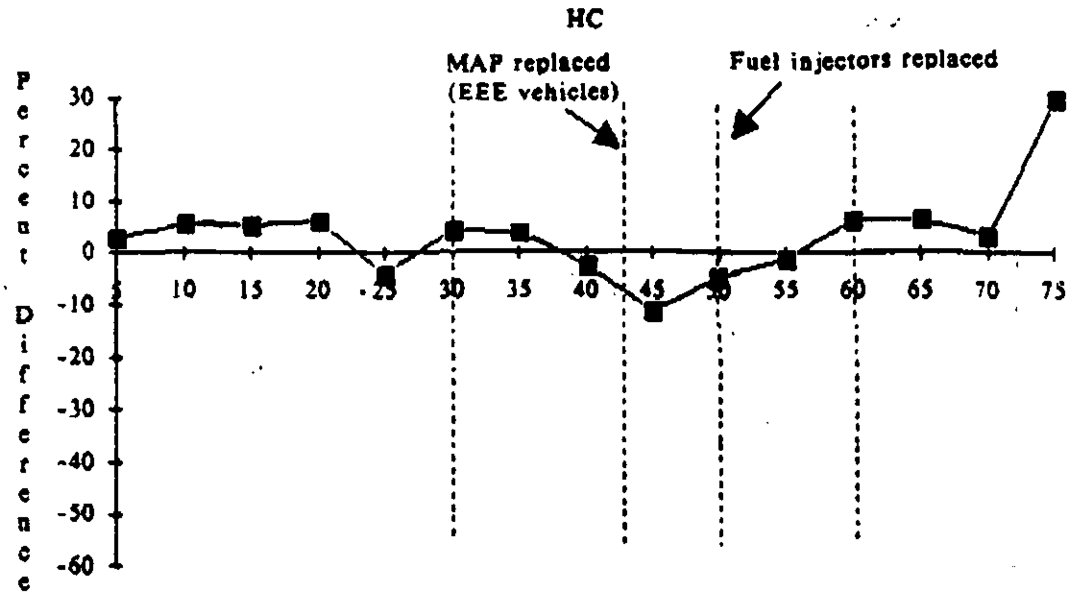


FIGURE 14

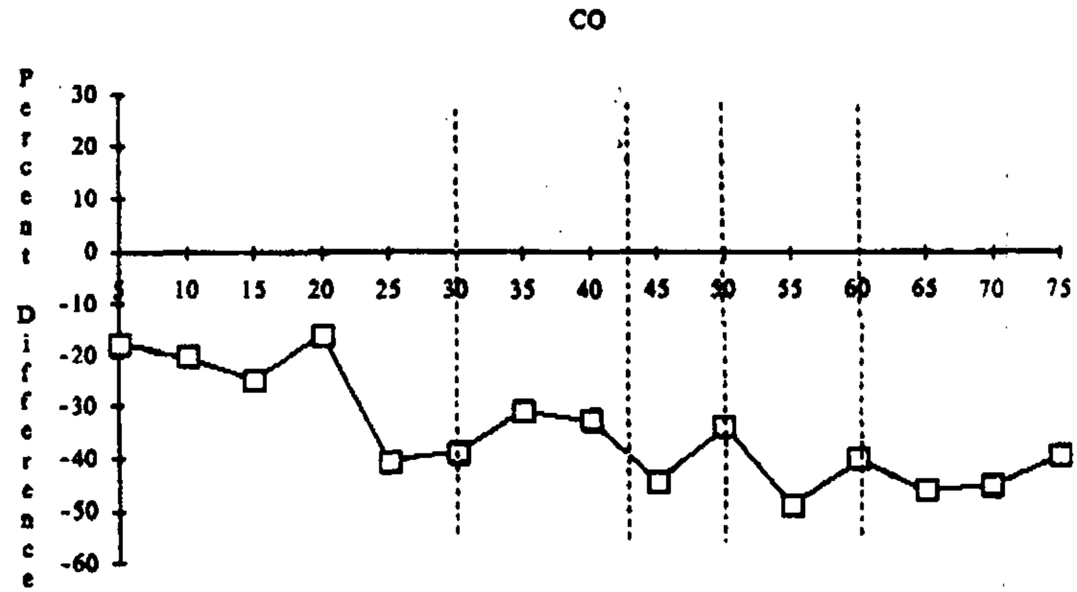
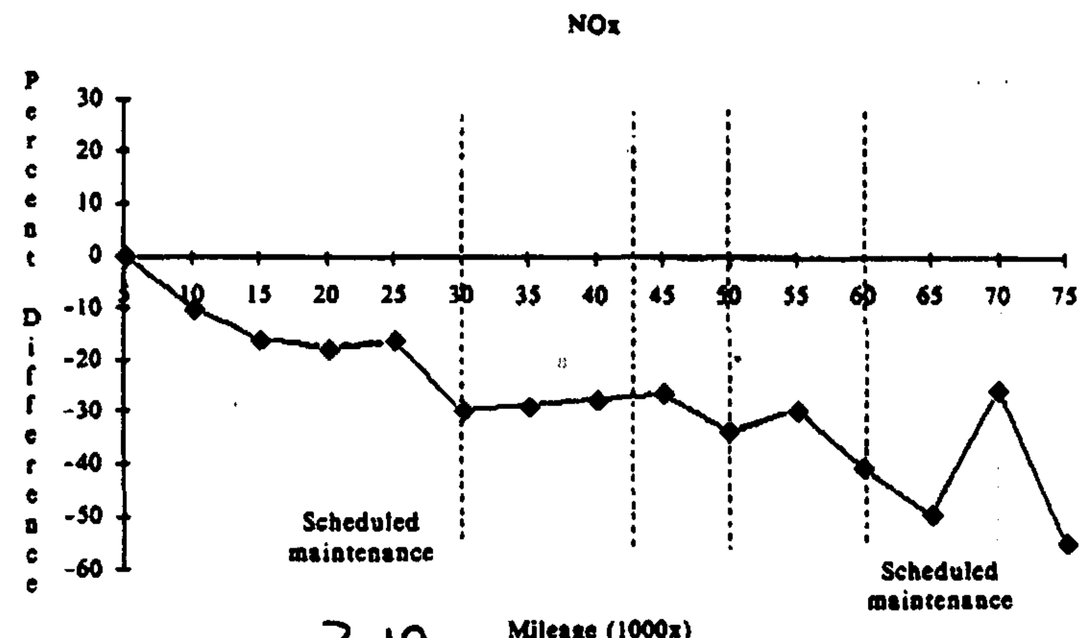


FIGURE 15



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Effects of MMT on Vehicle Emissions - Model G

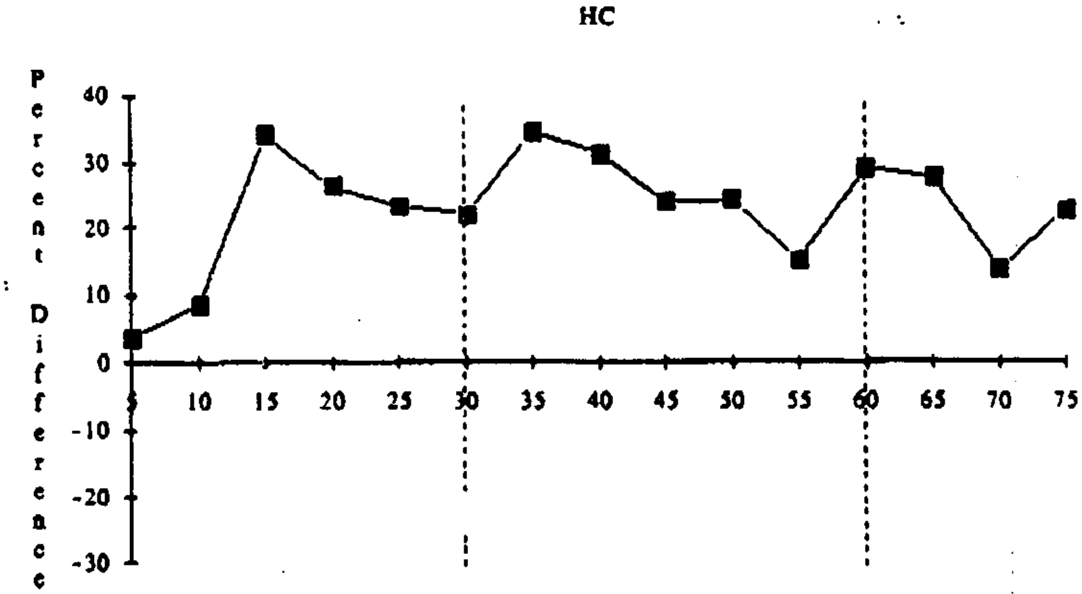
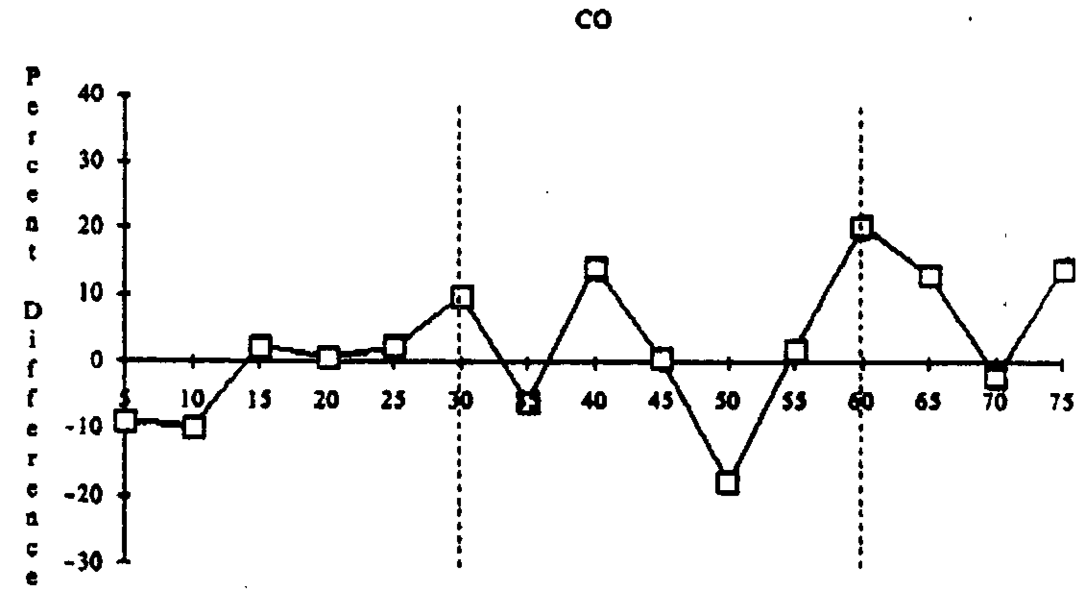


FIGURE 16



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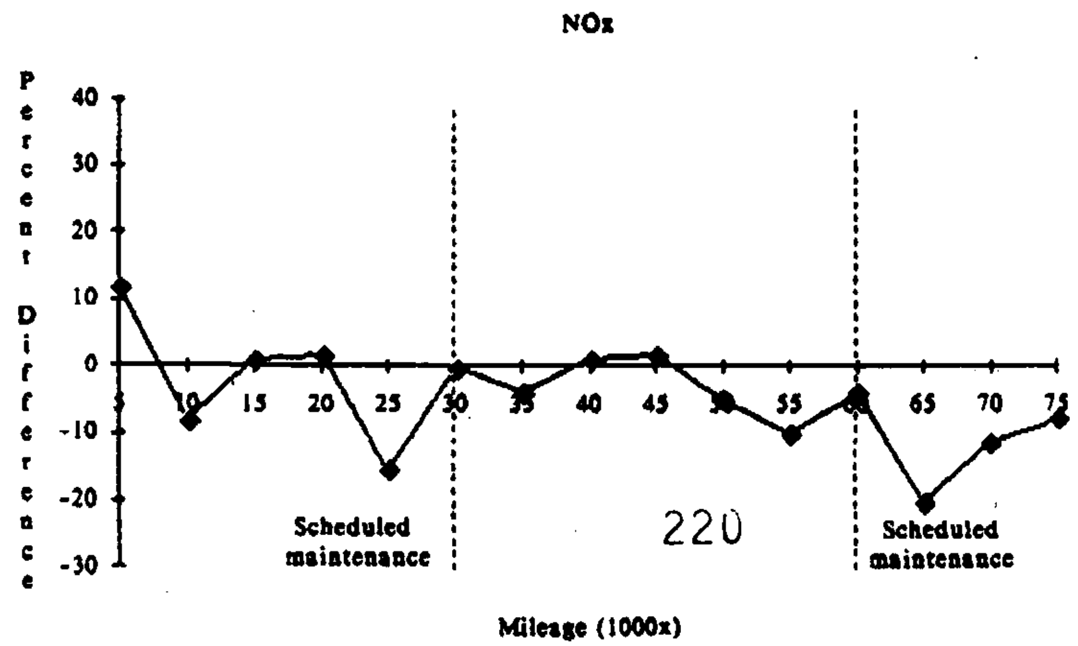
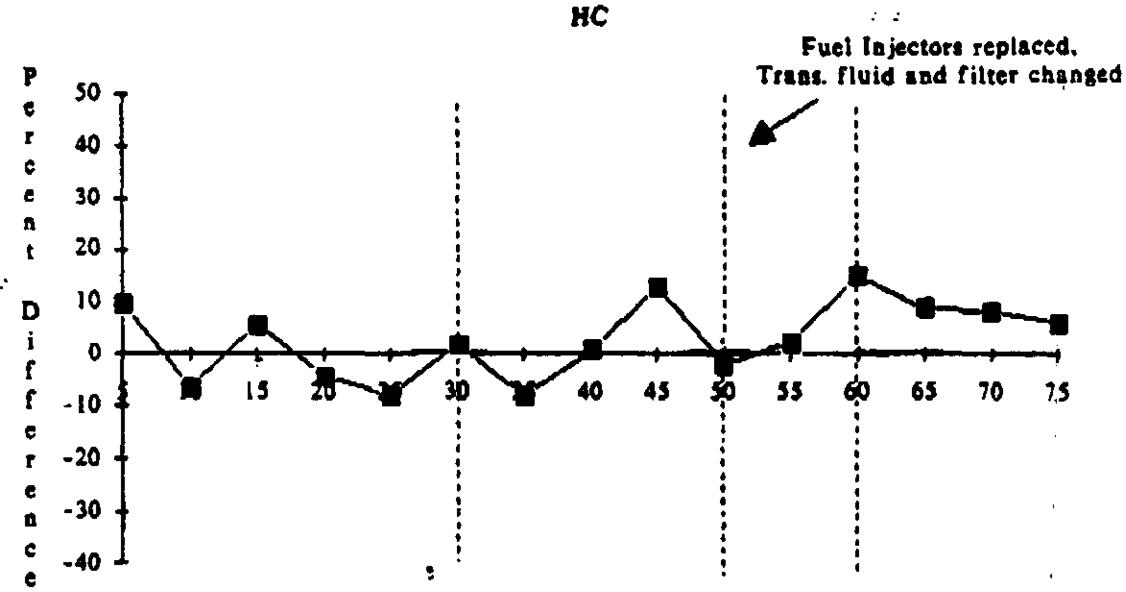


FIGURE 18

Effects of MMT on Vehicle Emissions - Model H

FIGURE 19



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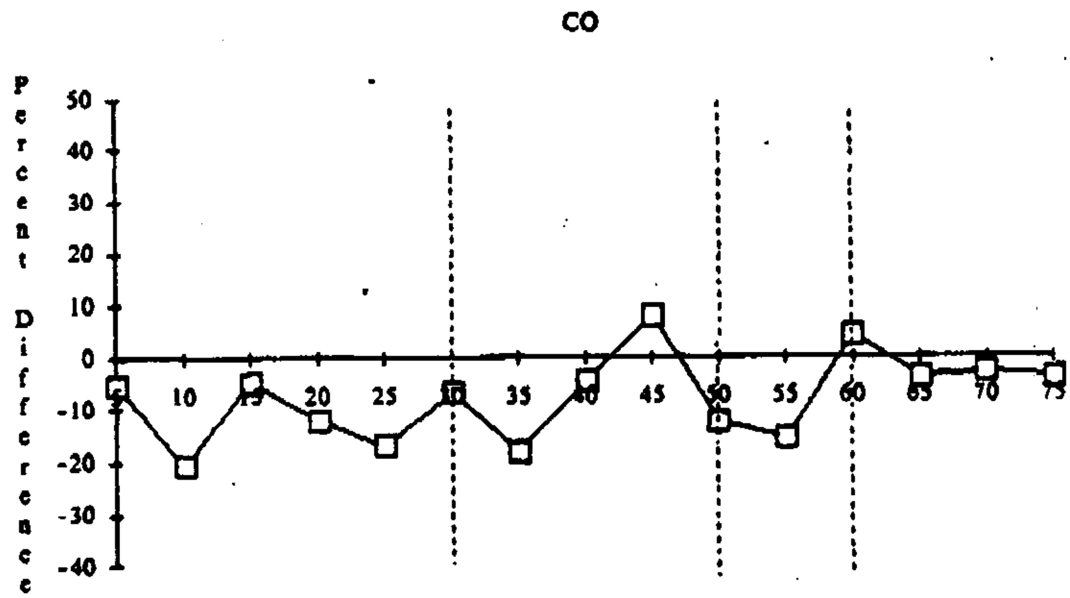

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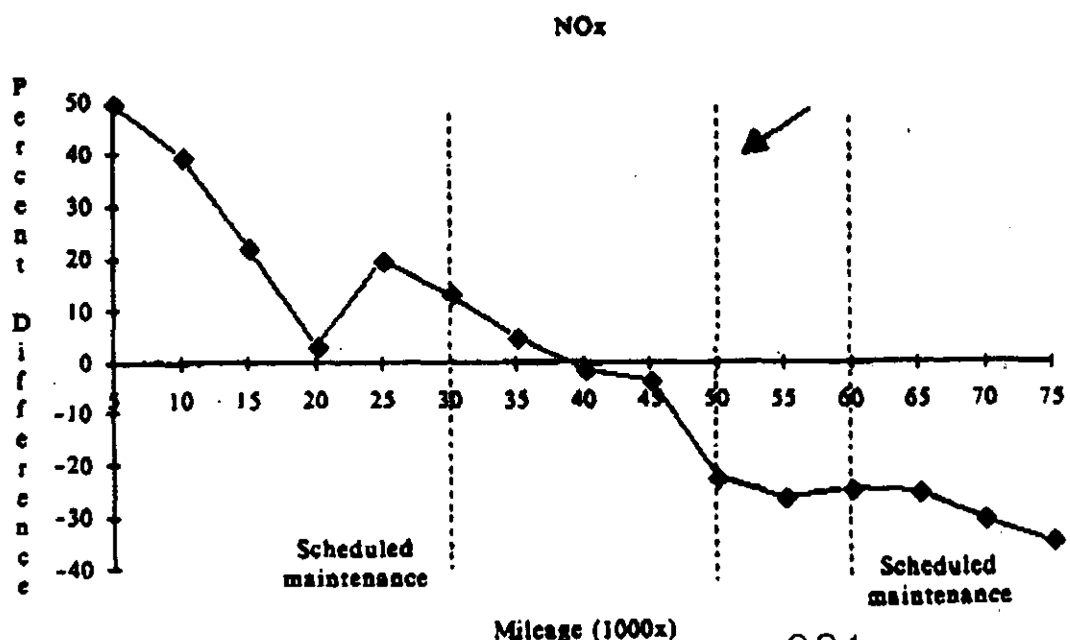
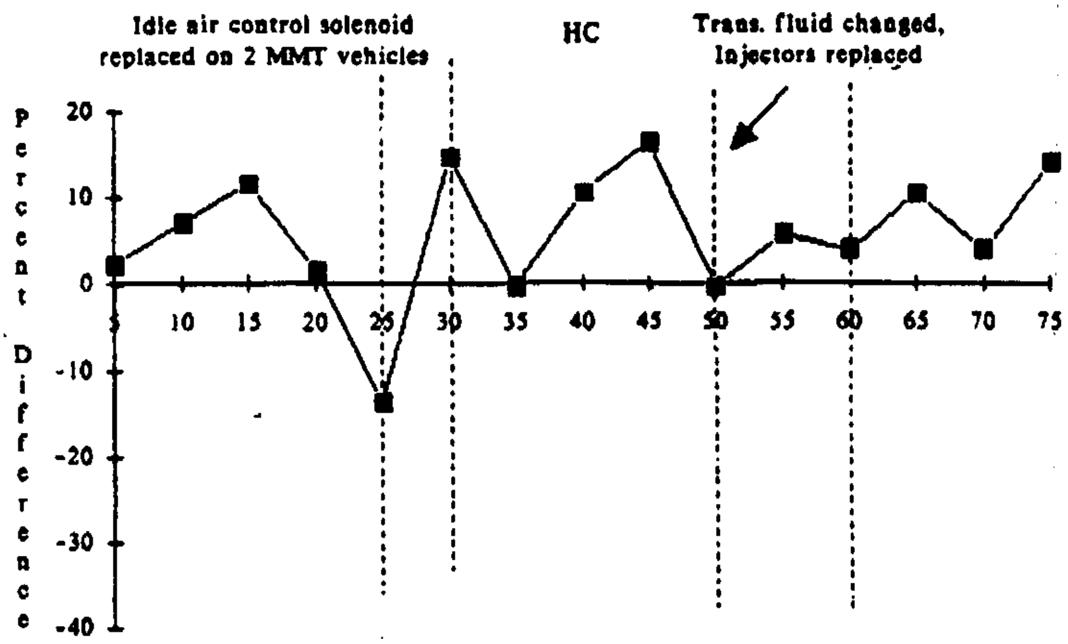


Effect of MMT on Vehicle 1

FIGURE 22



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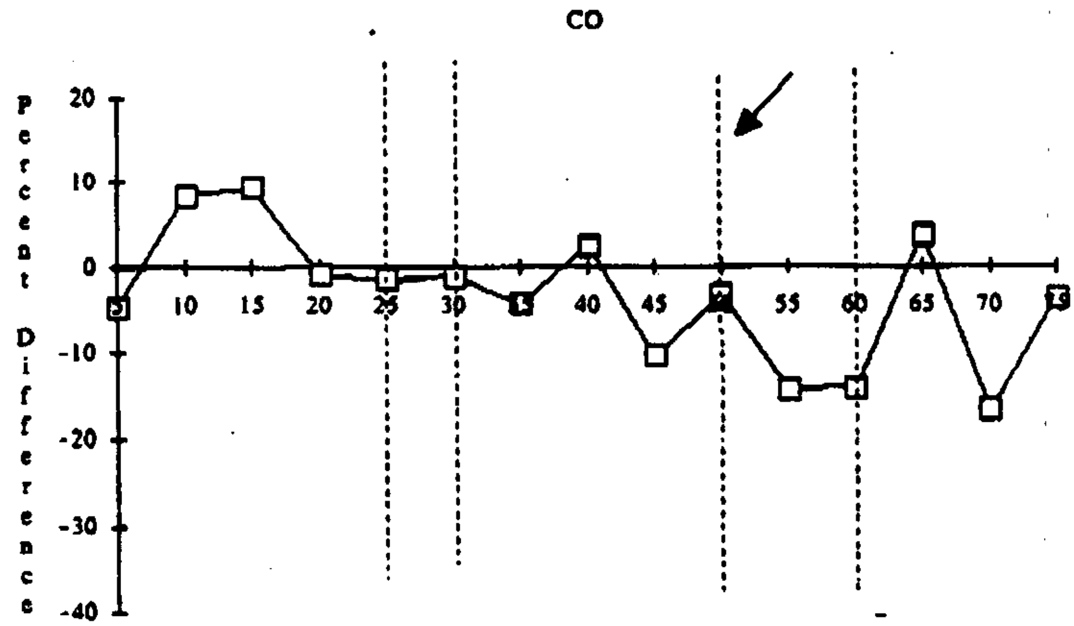
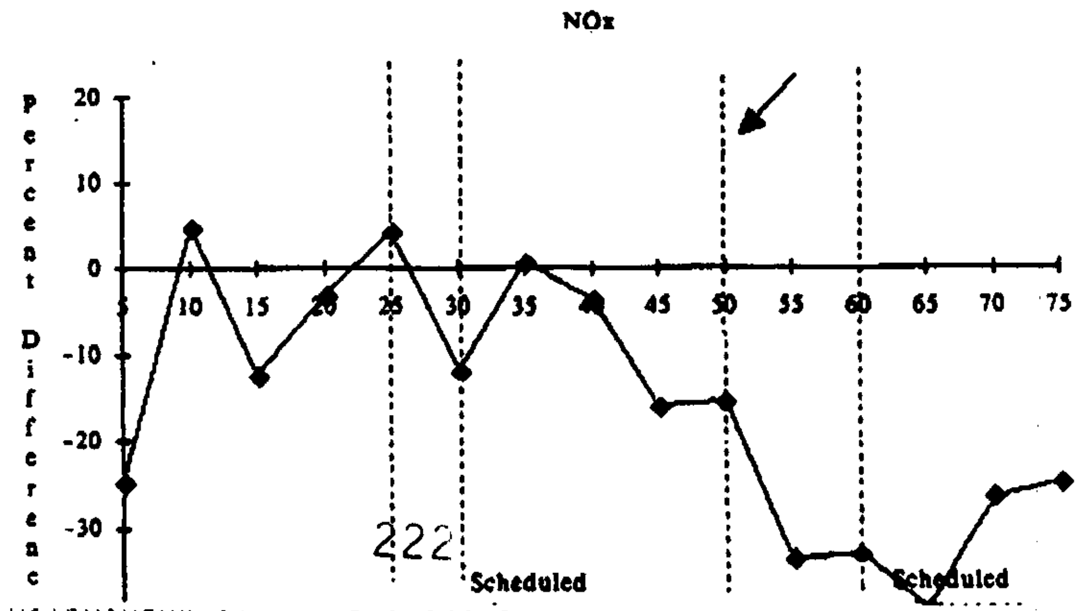


FIGURE 24



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Effects of MMT on Vehicle Emissions - Model T

FIGURE 25

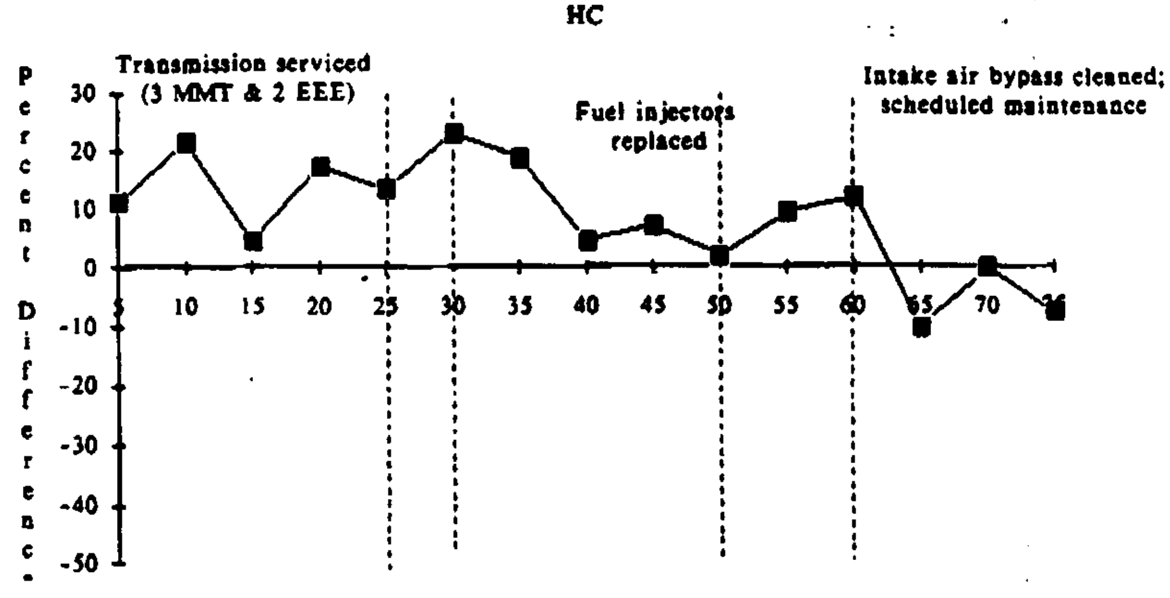


FIGURE 26

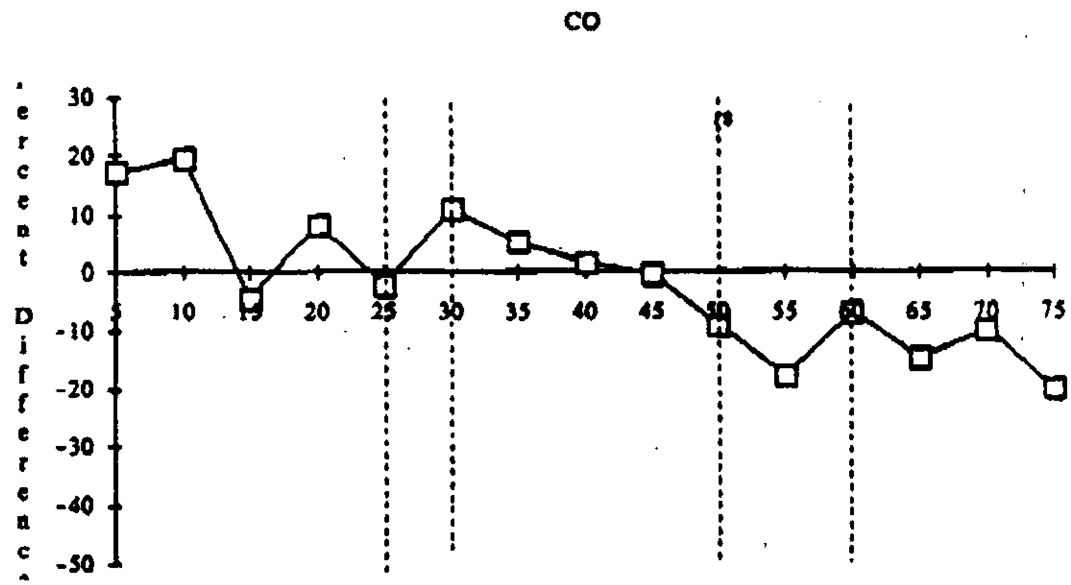
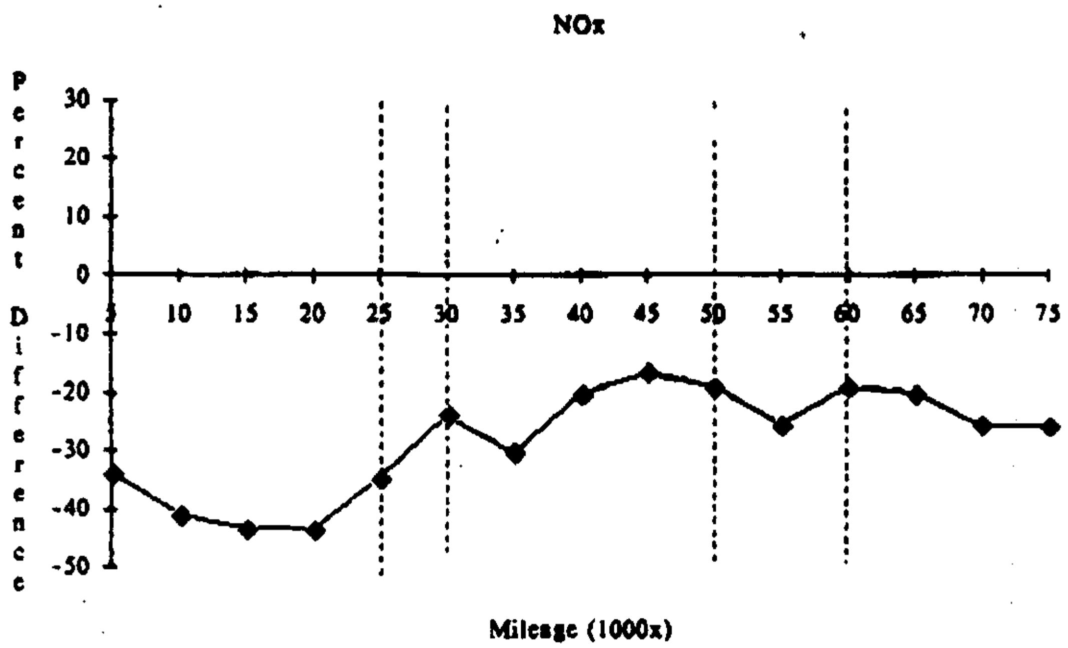


FIGURE 27



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Characterization of Automotive Catalysts Exposed to the Fuel Additive MMT

Ronald G. Hurley, William L. H. Watkins
and Robert C. Griffis
Ford Motor Co.

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Characterization of Automotive Catalysts Exposed to the Fuel Additive MMT

Ronald G. Hurley, William L. H. Watkins
and Robert C. Griffis
Ford Motor Co.

ABSTRACT

A series of in-use catalysts having mileage of 22,000 to 43,000 miles was characterized to determine the effect of the fuel additive MMT. The analytical techniques included visual examination, x-ray fluorescence, x-ray diffraction, optical microscopy, scanning electron microscopy, and electron microprobe. In addition, catalyst activity was measured and compared to the catalyst activity from a pulsator aged catalyst without the MMT additive in the feed gas composition. Characterization results show a significantly thick layer (5-20 microns) covering the surface of the catalysts which results in the increase of mass transfer resistance. Steady state R and light-off measurements indicated catalyst efficiency is also significantly reduced as exposure to MMT is increased.

In September, 1978 the addition of methylcyclopentadienyl manganese tricarbonyl (MMT) to gasoline fuel was denied by EPA. This denial was based on the failure to establish that the additive MMT would not cause or contribute to the failure of any 1975 or later model year vehicle to comply with applicable emission standards. In the meantime considerable experience has been accumulated in Canada where MMT at a concentration of 16.5 mg/l (1/16 g/gal) is added to fuel as an octane improver. The supplier of the octane improver, MMT, claims to have received no complaints regarding engine or exhaust system performance in approximately 400 billion in-use miles.

Considerable research has been done since the 1978 ruling on the use of MMT as a fuel additive (1-5). Wallace, et al. (5) and Benson, et al. (1) have shown that with 88% to 99% confidence that MMT adversely affects light duty vehicle tail pipe HC emissions at the MMT concentration 16.5mg/gal. Conversely, MMT did not statistically show a consistent adverse effect on CO or NO_x exhaust emission. Hughmark, et al. (4) conclude that MMT actually increases converter efficiency in relation to clear fuel. Williamson, et al. (2) concluded that the "catalyst enhancement phenomena" which resulted in the 2-3% HC improvement in catalyst efficiencies in the CRC study as well as the apparent beneficial effects observed in his research can perhaps be attributed to the scavenging effect or to catalytic activity of the MMT combustion product, Mn_3O_4(3). However, in each case the author examined the effects of MMT on emissions and did not particularly focus on the effects on the catalyst or determine the possible mechanism of catalyst deactivation. Consequently, and in response to the possibility of the EPA granting a waiver of the 1978 ruling and the subsequent use of an MMT additive in US gasoline, a study was undertaken to characterize, examine and evaluate a series of catalysts removed from in-use vehicles. The major objective of this paper, therefore, is to present an evaluation and characterization of the long term durability and efficiency of catalysts exposed to the fuel additive MMT.

EXPERIMENTAL

Nine (9) catalysts (Table 1) that had been exposed to MMT were removed from vehicles under warranty because of suspected converter defects. It should also be noted that these catalysts were taken from vehicles in which the authors had no means of verifying their fueling characteristics nor their proper function. Therefore, it was assumed by the authors that the vehicles used for this study were properly adjusted and fueled with gasoline that met the Canadian standard of 1/16 g/gal of MMT. As shown in Table 1 some of these converters were

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a two brick system and others were a single brick system. On the average these vehicles had accumulated 30,000 in-use miles. Characterizations performed consisted of visual examination, analysis by x-ray fluorescence (XRF), BET surface measurements, optical and scanning electron microscopic (SEM) examination of the washcoat conditions, contamination profiles and catalyst activity. Each of these analytical techniques is a standard post-mortem method for the characterization of in-use catalysts and will not be described in this paper.

Table 1

Vehicle Aged Catalysts Evaluated for Effects of MMT

No.	Engine Type	Model Year	Vehicle Type	Miles	Bricks
301-A	2.8L	1984	Bronco II	43K	2
301-B	2.3L HSC	1986	Topaz	24K	2
301-C	2.3L HSC	1985	Tempo	34K	1
301-D	1.9L 2V	1986	Lynx	22K	2
301-E	1.9L 2V	1985	Escort	28K	2
301-F	2.3L HSC	1984	Topaz	28K	1
301-G	2.3L HSC	1986	Tempo	22K	1
301-H	2.3L EFI	1985	Merkur	32K	2
301-I	2.3L OHC	1984	Ranger	33K	2

The catalysts received for evaluation, as shown in Table 1, were from 1984-1986 vehicles equipped with either 2.3L, 2.8L, or 1.9L engine. Each catalyst was sampled using standard techniques that have been described elsewhere in the literature (2). For x-ray fluorescence (XRF) the catalyst was cored and the resulting core divided into samples of inlet, middle, and outlet for analysis. Each sample consisted of approximately 6 grams of catalyst or sample plus corderite (fresh substrate) to approximate 6 grams. From a core portioned inlet, middle, and outlet a 0.5 gram sample from each was used for the standard BET analysis. Optical and scanning electron microscopic (SEM) samples were also selected in a similar manner as the XRF samples. For this analysis each inlet, middle and outlet sample was mounted and polished to provide a flat surface for analysis. Additional SEM samples were taken by breaking off portions of the catalyst, coating with a thin layer of gold or carbon to provide a conductive surface, and mounting on a carbon block for surface morphological examination. Samples for catalyst activity, steady state R and light-off analysis contained only the first 1/2 inch segment of inlet, middle, and outlet. Instrumentation for the MMT characterization included a SIEMENS SRS 300/VAX x-ray fluorescence spectrometer for XRF analysis. A QuantChrom Quantector Gas Flow System with a Quantasorb Flow Control Accessory was used for BET surface area measurements. The scanning electron microscope used in this characterization was an ETEC Autoscan equipped with a DELTA 3 Kevex energy dispersive x-ray system and a Kevex QUANTUM detector. Optical micrographs were taken using a Reichert metallograph for macros and a Neophote metallographs for micros. Steady state three-way activities and light-off curves were measured in a flow reactor over a range (lean-to-rich) of feed gas compositions.

RESULTS AND DISCUSSIONS

The typical as-received condition of the catalysts used in this study is shown in figure 1. Visually, the interior of the converters have a heavy to moderate coating of a rust colored residual deposit. Further visual inspection show that all of the catalyst cores have light to moderately heavy channel clogging of the inlet core of the first brick. Channel clogging of the catalyst core appears to be consistent and is limited to the first brick of the converter. Only one of the converters shows visual signs of exposure to high operating temperatures. This converter is shown in figure 2.

The results of x-ray fluorescence analysis of samples taken from each catalyst are shown in Table 2. These results summarize the concentration of the contaminants found to be present on the catalysts examined. Manganese concentration, as one might expect, is highest on the inlet of the catalyst and decreases toward the outlet. The Mn concentration range on the first brick, between a low of 1.4 wt% for a vehicle mileage of 24,000 to a high of 6.4 wt% for a vehicle having accumulated 33,000 in-use miles. The x-ray data are consistent with the visual examination in that the highest Mn concentration is limited to the first brick of the converter. The anomaly of Mn concentration reversal (low Mn on the inlet and higher on the outlet) as shown in 301D-1,-2 is due to exposure of this catalyst to high operating temperature which resulted in substantial substrate melting (figure 2). It is important to note that other contaminants S, P, Zn, and Pb, are generally in an acceptable range, somewhat higher than one might expect for this level of accumulated mileage. In addition, one might also expect that the Pb concentration would be higher than normal because of the possibility of the use of fuel from lower quality fuel refineries. This is evident in some of the catalyst but not to an extreme degree. The x-ray results are inconclusive in their tendency to confirm earlier studies that Mn_3O_4 acts as a scavenger (3) in the exhaust for transporting away fuel- and oil-derived catalyst poisons such as Pb, P, and Zn.

X-Ray diffraction analysis of the finely divided, rust colored deposits on the first brick indicates that this residual layer is primarily Mn_3O_4. These results confirm earlier experimental results (3,5) in that Mn derived

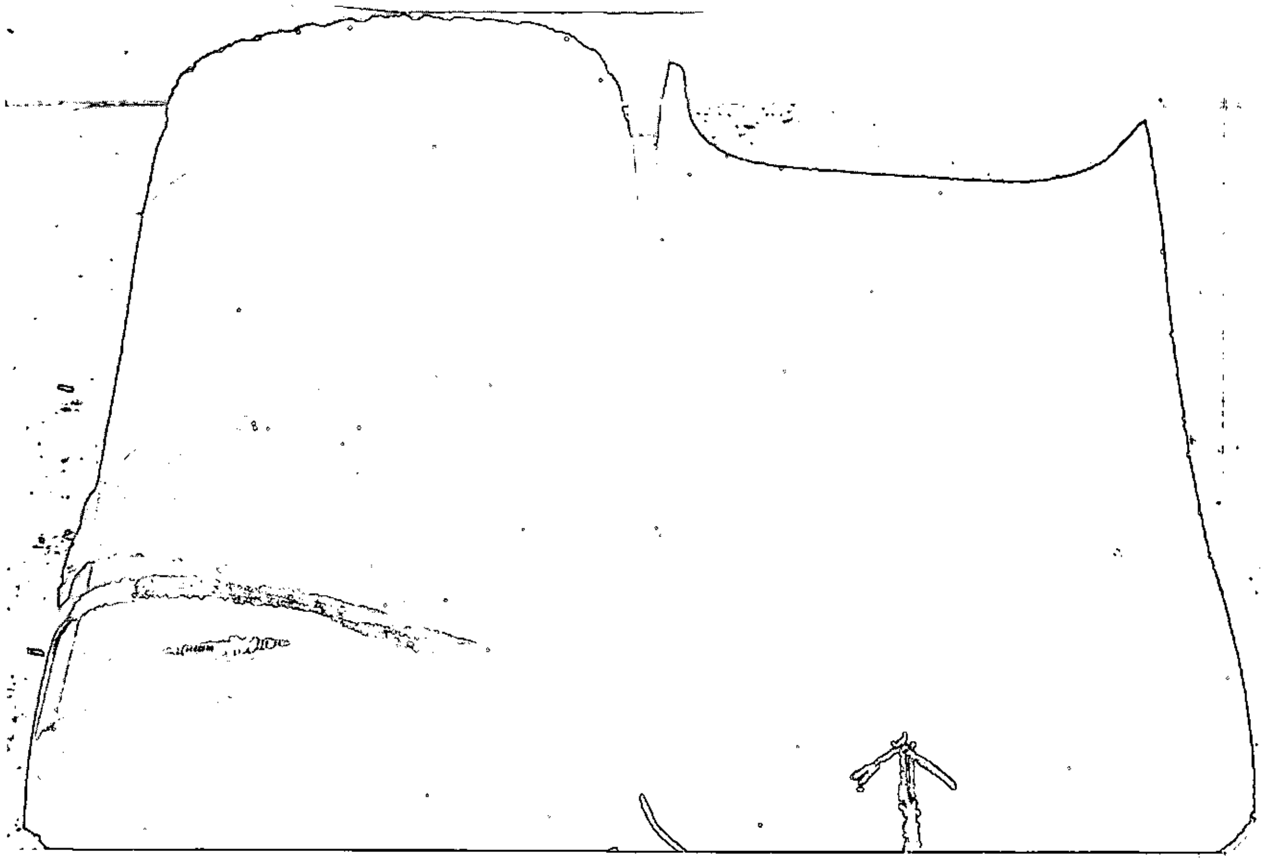

Figure 1. Example of the as-received condition of the in-use converters.

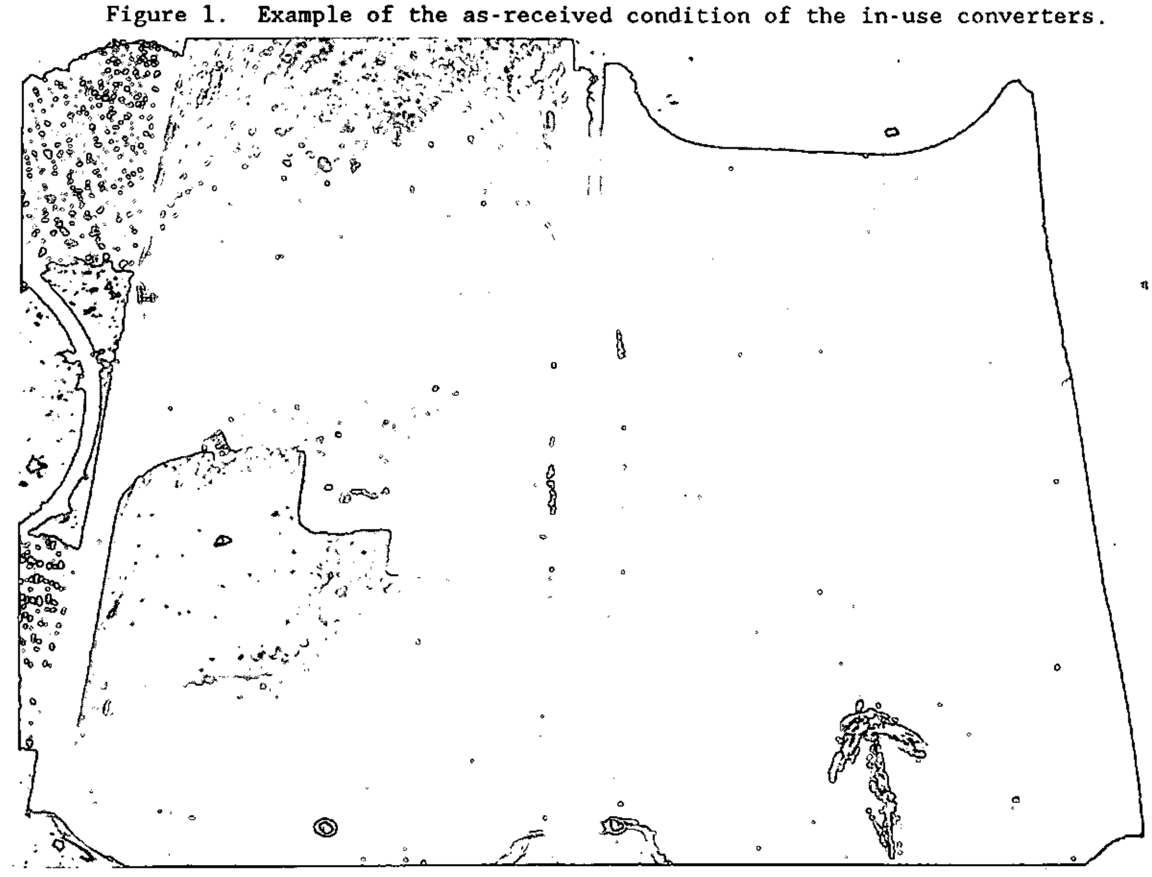

Figure 2. Example of in-use converter showing exposure to high operating temperature in the as-received condition.

Table 2
CONTAMINANT ANALYSIS OF AUTOMOTIVE CATALYSTS EXPOSED TO MMT

Vehicle Catalyst		Miles	Type	Contaminants, Wt% Mn	S	P	Zn	Pb
301A-1	I	43,000	TWC	2.08	0.0	.46	.14	.67
	M			.83	0.0	.16	.05	.04
	O			.53	0.0	.10	.03	.07
301A-2	I		COC	.83	0.0	.16	.06	.21
	M			.28	0.0	.06	.02	.12
	O			.26	0.0	.05	.01	.12
301B-1	I	24,000	TWC	1.43	.14	.13	.12	.07
	M			.37	.12	.06	.03	.03
	O			.35	.12	.06	.02	.06
301B-2	I		COC	.48	.21	.08	.02	.04
	M			.19	.20	.04	.01	.02
	O			.16	.16	.04	.01	.01
301C	I	34,000	TWC	5.20	.14	.39	.28	.41
	M			2.57	.05	.25	.13	.22
	O			2.24	.03	.23	.10	.21
301D-1	I	22,000	TWC	.79	.0	.07	.02	.03
	M			.80	.0	.06	.01	.02
	O			2.18	.01	.18	.09	.19
301D-2	I		COC	1.62	.16	.11	.01	.07
	M			.69	.02	.06	.01	.23
	O			.60	.06	.06	.02	.13
301E-1	I	28,000	TWC	1.77	.05	.18	.08	.54
	M			.91	.05	.09	.02	.02
	O			1.08	.08	.09	.02	.02
301E-2	I		COC	1.76	.12	.13	.04	.30
	M			.86	.10	.08	.01	.34
	O			.77	.11	.07	.01	.49
301F	I	28,000	TWC	3.15	.11	.22	.20	.74
	M			2.14	.06	.11	.11	.46
	O			1.76	.05	.10	.08	.37
301G	I	22,000	TWC	4.20	.26	.27	.24	.22
	M			2.05	.11	.19	.13	.09
	O			1.58	.14	.15	.09	.06
301H-1	I	32,000	TWC	1.72	.12	.24	.25	.02
	M			.92	.13	.12	.11	.03
	O			.75	.12	.10	.07	.03
301H-2	I		COC	.81	.12	.11	.08	.04
	M			.51	.13	.06	.04	.03
	O			.41	.14	.06	.03	.03
301I-1	I	33,000	TWC	6.14	.02	.63	.58	.52
	M			2.70	.0	.29	.13	.14
	O			1.98	.0	.25	.11	.08
301I-2	I		COC	3.39	.0	.37	.28	.33
	M			1.71	.0	.18	.06	.09
	O			1.49	.0	.16	.04	.11

from MMT is converted in the combustion process exclusively to Mn_3O_4.

Optical micrographs (figures 3 and 4) of catalysts, 301G and 301I, show a heavy residual layer covering the washcoat. X-Ray fluorescence results indicate that these two samples, contain approximately 4 and 6 wt% of Mn, respectively and are from vehicles with 22,000 and 33,000 accumulated in-use miles. As is evident in both of the high magnification micrographs, from 301G and 301I, the Mn_3O_4 is on layered on the surface of the washcoat. It does not appear to penetrate or have reacted with the washcoat but simply adheres to the surface. This deposit of Mn_3O_4 on the washcoat may cause physical pore plugging and thus result in mass-transfer problems.

Scanning Electron Microscopic and Electron Probe analysis show the thickness of the Mn_3O_4 residual layer to range from approximately 5 microns to a maximum of approximately 20 microns. The thickest layer is observed on catalyst 301I which had 33,000 accumulated miles. SEM micrographs (figure 5) of cross-sections of 301G and 301I show this layer quite distinctly. Also shown in this figure is a Mn x-ray elemental map pattern to confirm that the layer is indeed rich in Mn. This elemental map is used to determine the actual thickness of the Mn rich region on the washcoat. This micrographs also indicate little if any penetration into the washcoat by the Mn rich layer. Indications from the surface morphology study is that the Mn rich layer does simply adhere to the surface of the washcoat. An example of the surface morphology of the Mn rich layer is shown in figure 6. As is shown in the micrograph the surface is covered with a layer of fluffy, porous material. This material was confirmed by XRD to consist exclusively of Mn_3O_4.

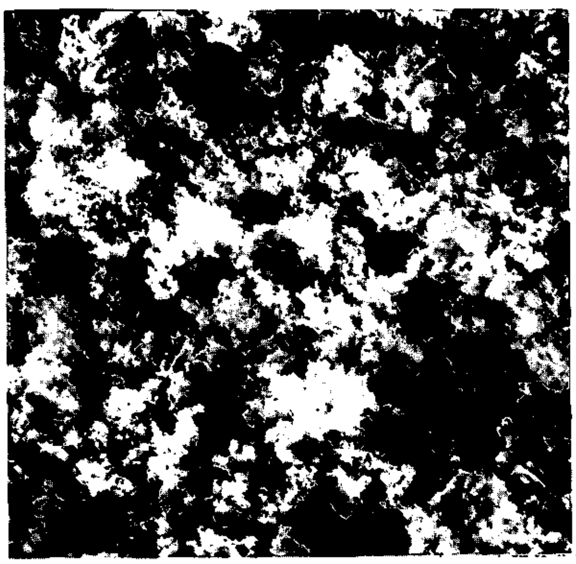

Figure 6. Surface morphology of Mn rich layer on 33,000 mile MMT exposed catalyst.

BET surface areas (Table 3) range between 14.0 m^2/gm and 0.9 m^2/gm for the first brick and between 9.3 m^2/gm and 0.6 m^2/gm for the second brick. In general, as shown in Table 3, all the surface area measurements were lower than that of a fresh catalyst's surface area of approximately 25 m^2/gm. The lower BET values measured for the catalysts could be due to two mechanisms: 1) exposure to higher than normal operational temperatures and 2) the reduction of active surface area sites by the heavy coating of Mn_3O_4. However, there is no prior experimental evidence that the combustion products of MMT reduces "active surface area sites". Most likely the Mn_3O_4 deposits cause pore plugging and subsequent mass transfer problems. This diffusion hinderance would certainly be reflected in a erroneous decrease of the BET areas, if measured by one-point dynamic desorption.

Conversion efficiencies were measured for two of the MMT exposed catalysts, 301G and 301I having accumulated 22,000 and 33,000 miles, respectively. In addition, a comparison of the catalyst efficiency was made between a pulsator aged catalyst and the MMT exposed catalysts. The pulsator aged catalyst was aged with a "low-lead" (no MMT) simulated certification fuel, i.e., isooctane containing 2 mg Pb + 0.8 mg P + 0.03 wt % S/gal, to the equivalent of 15,000 miles. The activity and three-way selectivity of catalysts is expressed as percent conversion of NO, CO, and HC against the redox ratio (R) of the reacting gas mixture. These points are plotted over a range of rich to lean air fuel ratio to obtain an R curve. Optimum selectivity and redox ratio values corresponding to the peak three-way conversion point are determined by interpolation from resulting curves. As shown in equation below, R is obtained by dividing the sum of the equivalent reducing components of the mixture by the sum of the oxidizing components. Thus

$$R = \frac{pCO + pH_2 + 3nC_nH_2n + 3.33npC_nH_{2n} + 2}{pNO + 2pO_2}$$

Therefore a value of R > 1 represents an overall reducing gas mixture and a value of R = 1 represents a stoichiometric gas mixture. The redox ratio, a measure of the exhaust stoichiometry and related to the A/F ratio, is a measure of the fuel mixture stoichiometry. It is a more sensitive yardstick, since, in the exhaust, most of the mixture has been burned away. Steady-state R curves (measure of catalyst conversion efficiency with respect to HC, NO, and CO) and light-off temperatures were measured on a flow reactor over a range (lean-to-rich) of feed gas composition. A comparison of steady-state R curve data (figure 7) between the MMT exposed and a non-MMT exposed catalyst indicate equal deterioration among the three catalysts for CO activity. However, there was

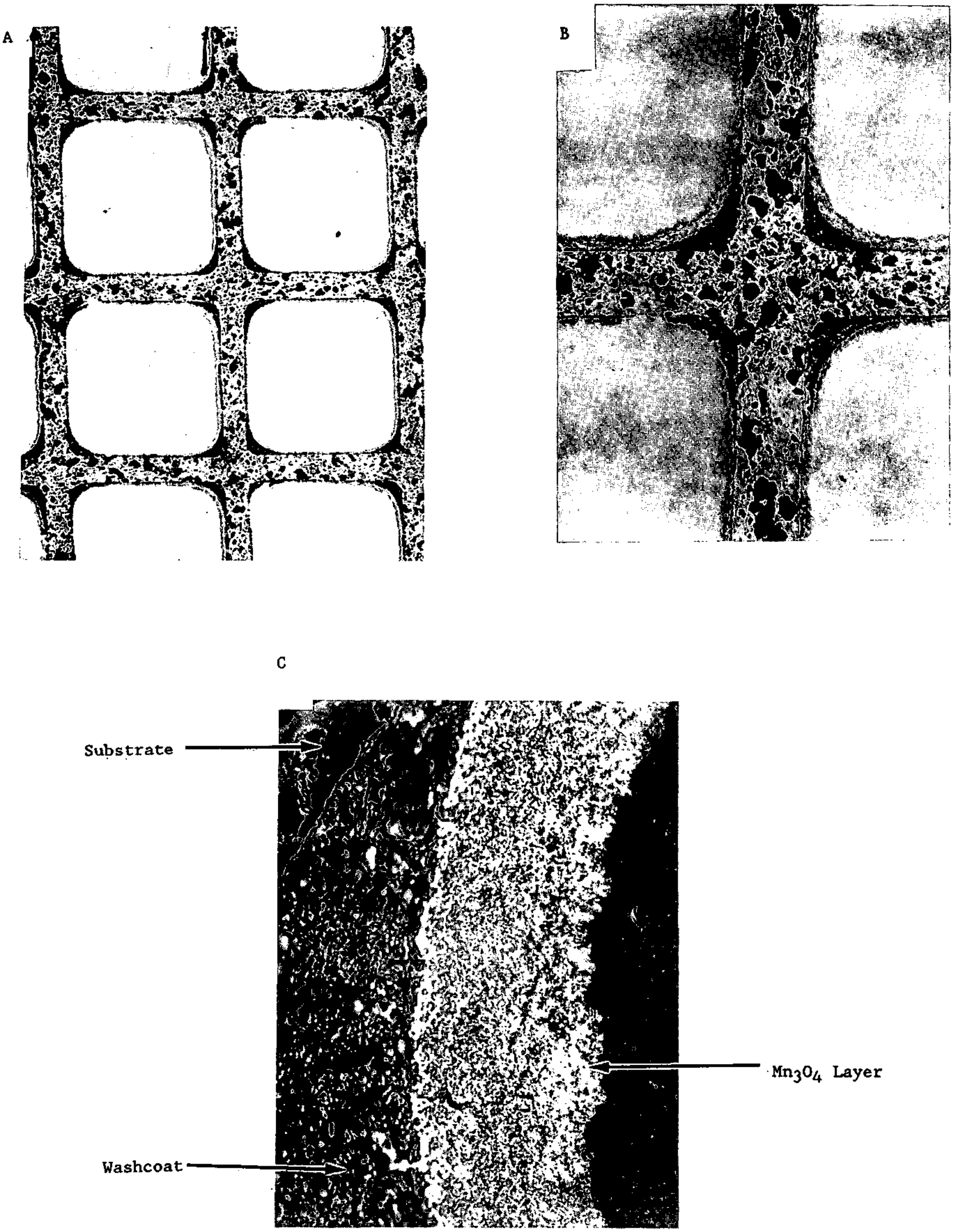

Figure 3. Optical Micrographs of 33,000 mile MMT exposed catalyst TC-301I at (a) 30X, (b) 80X, and (c) 800X.

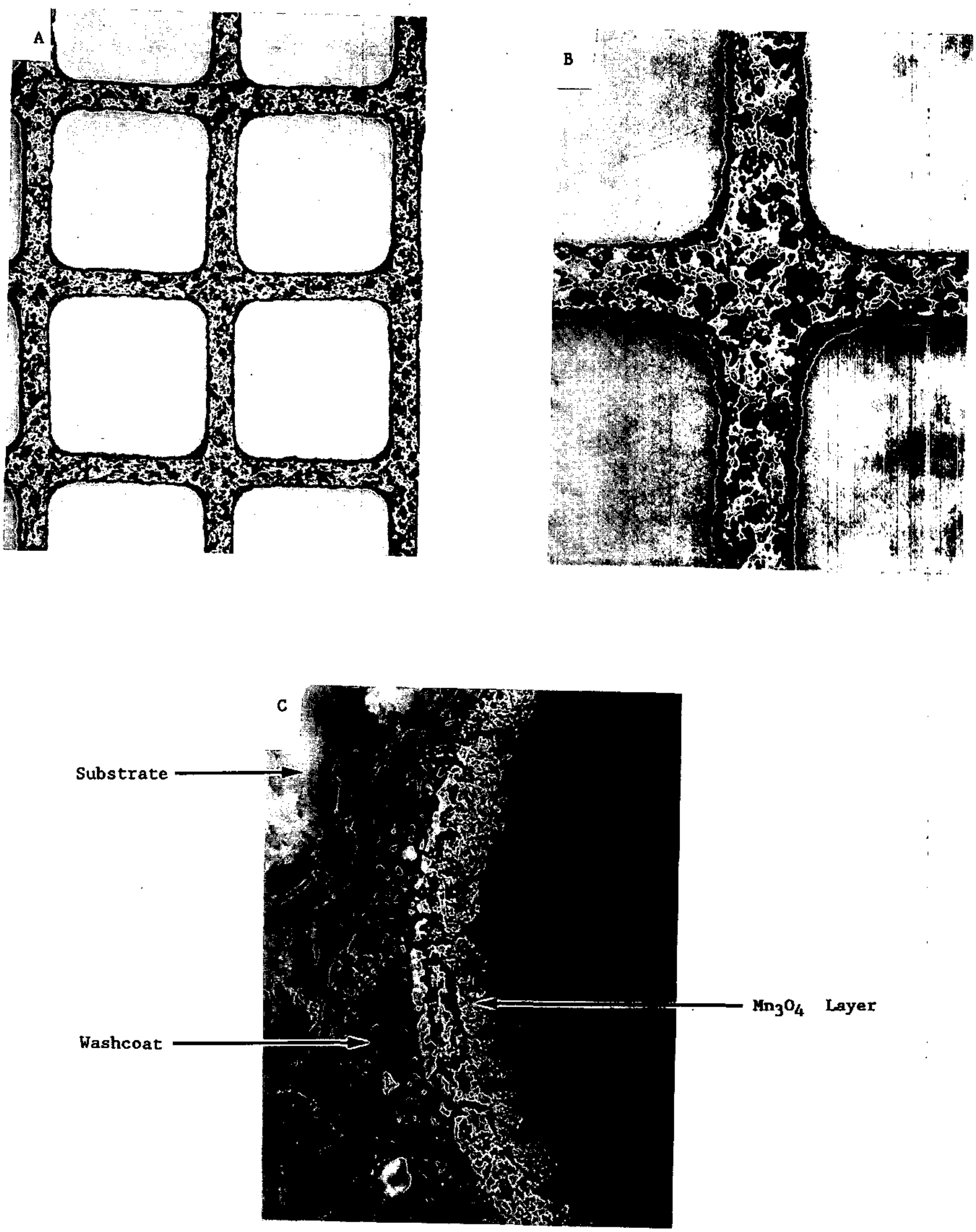

Figure 4. Optical micrographs of 22,000 mile MMT exposed catalyst TC-301G at (a) 30X, (b) 80X, and (c) 800X.

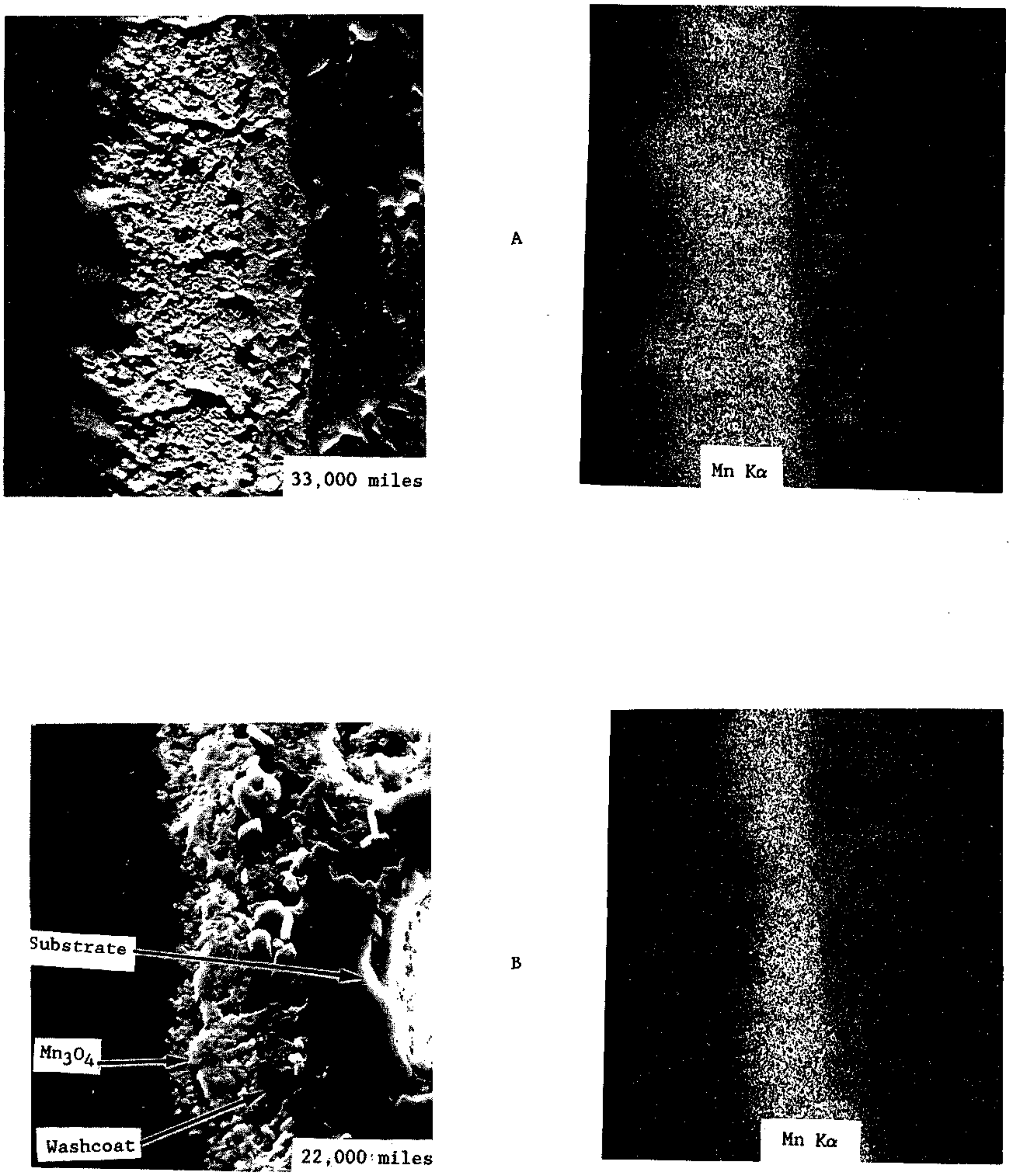

Figure 5. Scanning electron micrographs and Mn Kα elemental maps of (a) 33,000 miles MMT exposed catalyst and (b) 22,000 miles MMT exposed catalyst. (1 cm = 10 microns).

Table 3

B.E.T. SURFACE AREA MEASUREMENT OF AUTOMOTIVE CATALYSTS EXPOSED TO MMT

Vehicle Catalysts		Type	Miles	B.E.T. Area (M^2/g)
301A-1	I	TWC	43,000	3.8
	M			6.8
	O			4.5
301A-2	I	COC		2.7
	M			4.1
	O			4.0
301B-1	I	TWC	24,000	13.9
	M			15.4
	O			12.8
301B-2	I	COC		7.6
	M			8.7
	O			8.2
301C	I	TWC	34,000	8.5
	M			7.4
	O			7.0
301D-1	I	TWC	22,000	.8
	M			.5
	O			1.3
301D-2	I	COC		.3
	M			.7
	O			4.0
301E-1	I	TWC	28,000	4.4
	M			5.6
	O			5.5
301E-2	I	COC		6.9
	M			7.9
	O			8.6
301F	I	TWC	28,000	14.1
	M			12.4
	O			11.0
301G	I	TWC	22,000	7.3
	M			6.7
	O			6.6
301H-1	I	TWC	32,000	8.9
	M			9.8
	O			9.8
301H-2	I	COC		8.4
	M			10.2
	O			9.3
301I-1	I	TWC	33,000	3.8
	M			4.0
	O			4.3
301I-2	I	COC		1.2
	M			0.4
	O			0.3

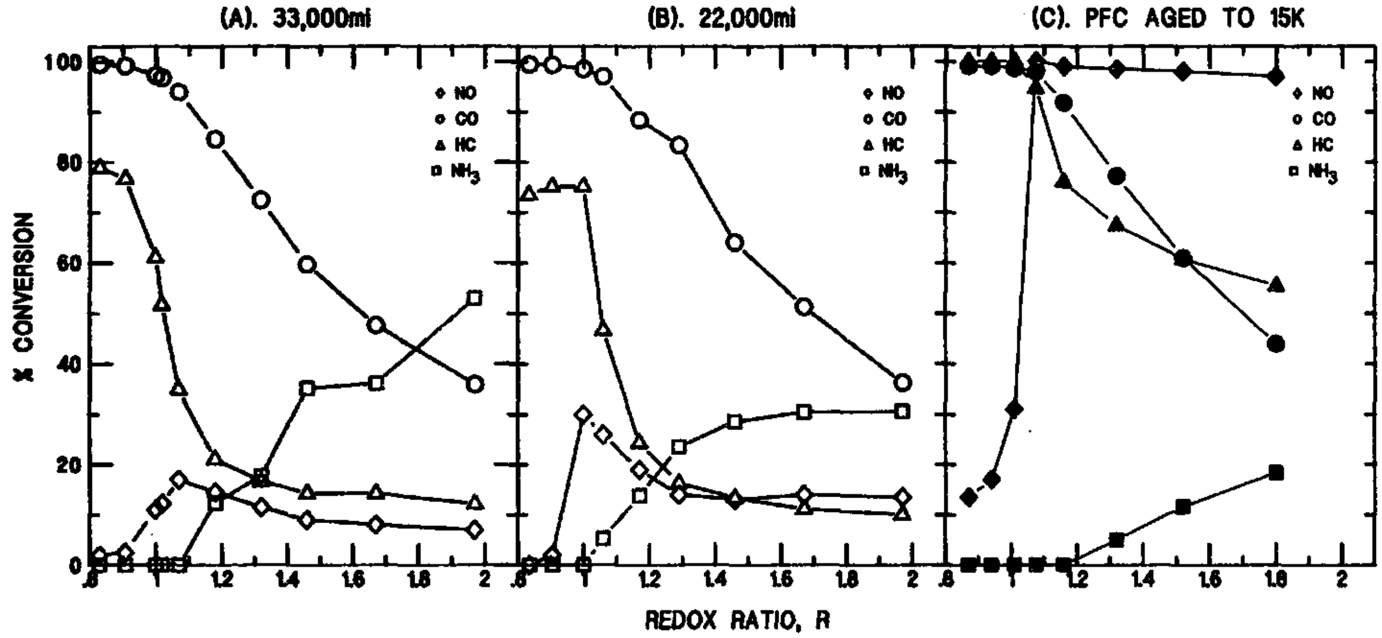

Figure 7. Comparison of the steady-state NO, CO, and HC activities for (a) 33,000 miles MMT exposed catalyst, (b) 22,000 miles MMT exposed catalyst, and (c) 15,000 mile non-MMT pulsator aged catalyst.

extreme deterioration of NO and HC activity for the MMT exposed catalysts. The peak NO conversion as measured at an R value of 1.07 was 100%, 27%, and 15% for the pulsator aged catalyst and the MMT catalysts 301G, 301I, respectively. The peak HC conversion at an R value of 1.07 was measured to be 95%, 43%, and 32% for the pulsator aged catalyst and the MMT catalysts 301G, 301I, respectively. In addition, the data indicate that NH_3 formation increases as the catalyst is exposed to MMT. This is understandable because Mn_3O_4 is not a selective catalyst to reduce NO to N_2.

A comparison of steady-state light-off curve data (figure 8) between the MMT exposed and a non-MMT exposed catalyst show 80% conversion for HC, CO, and NO for the pulsator (non-MMT) catalyst to be at approximately 280° C. Whereas 80% conversion for CO was approximately 410° C for catalyst 301G and approximately 460° C for catalyst 301I. Eighty (80) percent conversion does not take place for HC or NO for either MMT exposed catalyst. The curves also show that 50% conversion of HC, CO, and NO takes place at approximately 250° C for the pulsator aged catalyst. Fifty (50) percent conversion for CO and HC takes place at 350° C and 460° C, respectively, for catalyst 301G. Likewise, 50% conversion of CO and HC takes place at 400° C and 530° C, respectively, for catalyst 301I. The data indicate that 50% conversion does not take place for NO on either of the MMT exposed catalyst.

CONCLUSIONS

Although the authors had no means of verifying the fueling characteristics of the vehicles nor the proper function of the vehicles from which the catalysts were taken, the conclusions are based on the assumption that these vehicles were properly adjusted and fueled with gasoline containing 1/16 g/gal MMT. The following salient results obtained from the post-mortem analysis of these catalysts can be summarized as follows:

- Minor to severe clogging of the first brick by the residue of the oxidation product of MMT, Mn_3O_4,
- 5-20 micron thick layer of Mn_3O_4 over the washcoat surface,
- decrease in surface area (BET) measurements,
- percent conversion of NO, CO, and HC decreases as the exposure to MMT increases,
- NH_3 formation increases as the exposure to MMT increases, and,
- light-off temperatures for NO, CO, and HC increase as the exposure to MMT increases.

The mechanism of deactivation as determined by this analysis is due to the clogging of the

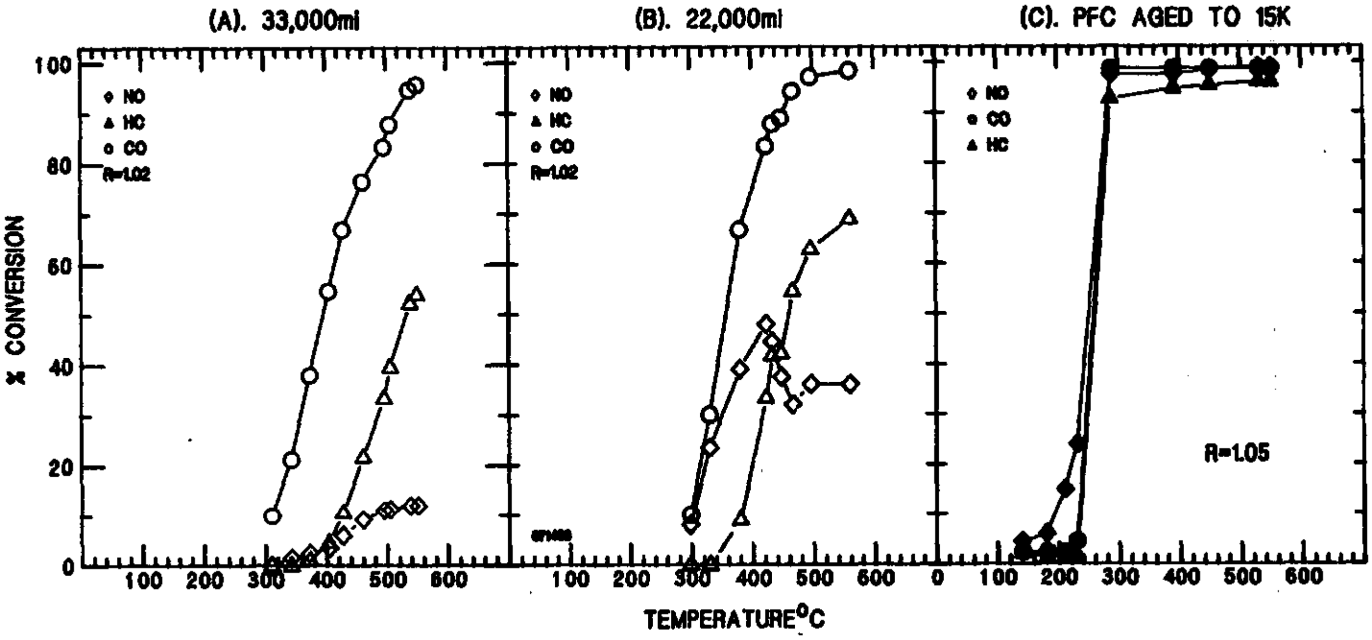

Figure 8. Comparison of the light-off NO, CO, and HC activities for (a) 33,000 miles MMT exposed catalyst, (b) 22,000 miles MMT exposed catalyst, and (c) 15,000 mile non-MMT pulsator aged catalyst.

channels of the converter. This plugging of the channels of the monolith results in an increase of the mass transfer resistance and consequently reduces the efficiency of the catalyst to convert HC, CO and NO_x. Based on these results it appears that the fuel additive MMT had a deleterious effect on the efficiency of the catalysts tested. However, in order to access more definitively the effect of MMT on in-use vehicle catalyst efficiency, this study suggests the need to correlate cause and effect from vehicles fueled with and without the fuel additive MMT.

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